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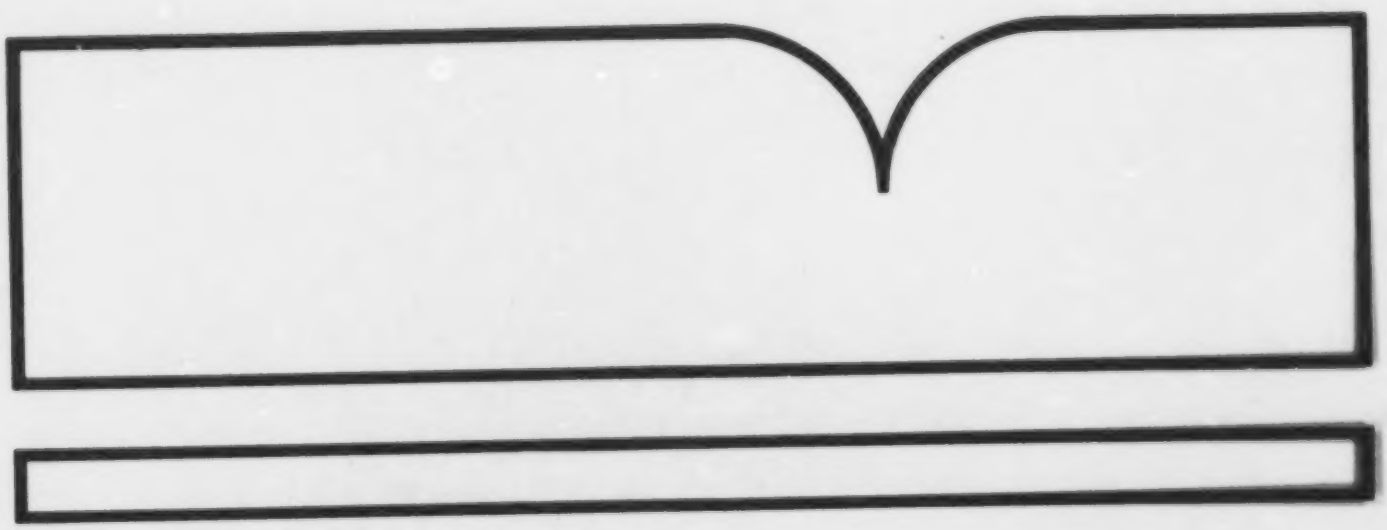

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A Survey of Plasticizers: Epoxies, Linear Polyesters, and Trimellitates

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Study investigated the published literature for selected areas in three classes of plasticizers: epoxies, linear polyesters, and trimellitates. Areas of interest included physical and chemical properties, production and use, health and environmental effects, and plasticizer interchangeability. Current production methods, sites, and annual volumes are presented for each class. Little information is available in the published literature on health effects. No occupational standards exist for any of the three classes. Unpublished health data are available for selected tests from manufacturers for specific materials. Environmental effects were limited to static fish toxicity studies for two trimellitates and studies of fungal and bacterial growth with epoxies and linear polyesters. Both classes of plasticizers are very susceptible to fungal and bacterial attack.

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Task VI - A Survey of Plasticizers: Epoxies, Linear Polyesters, and Trimellitates

FINAL REPORT
November 1981

EPA Contract No. 68-01-3896
MRI Project No. 4441-T(6)

For

Environmental Protection Agency
Office of Toxic Substances
401 M Street, S.W.
Washington, D.C. 20460

Attn: Mr. Roman Kuchkuda
Project officer

NOTICE

This report has been reviewed by the Office of Toxic Substances, Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency. Mention of trade names or commercial products is for purposes of clarity only and does not constitute endorsement or recommendation for use.

PREFACE

This report presents the results of a study to compile and analyze published information for three classes of plasticizers: epoxy compounds, linear polyesters, and trimellitates.

This study was performed by Midwest Research Institute as Task VI under Contract No. 68-01-3896 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. Project officer for this study was Mr. Roman Kuchkuda. Midwest Research Institute contributors to this study were: Dr. Thomas W. Lapp (Task Leader), Mr. Charles E. Mumma, and Mr. Joseph Chaszar. This contract is being performed under the supervision of Mr. Thomas L. Ferguson, Head, Process Analysis Section.

Midwest Research Institute would like to express sincere appreciation to the many industry sources who provided technical input to this study, especially to Mr. J. T. (Jack) Lutz and Mr. J. E. Voit of Rohm and Haas Company, Mr. Robert Radue of Monsanto Company, and Mr. Jesse Edenbaum of Technor-Apex for their valuable assistance.

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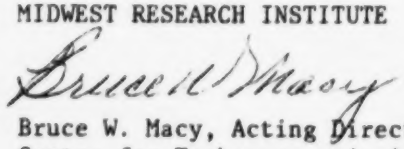

Bruce W. Macy, Acting Director
Center for Technoeconomic Analysis

November 10, 1981

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SECTION I

INTRODUCTION

Plasticizers are an integral component of many current thermoplastics. This component imparts workability, flexibility, extensibility, and resilience to the final product. Over 80% of all plasticizers for thermoplastics are used with polyvinyl chloride (PVC); over 90% of the plasticizers under study in this report are used in PVC. The entire classification of plasticizers entails a wide range of compounds, most of which are esters of long-chain (C_5 or higher) acids. The Environmental Protection Agency, Office of Pesticides and Toxic Substances (OPTS), is currently reviewing the various materials employed as plasticizers and compiling information on these compounds so that their relative importance may be evaluated.

Two major classes of plasticizers, triaryl and alkylaryl phosphate esters and alkyl phthalate esters, have been or are currently under extensive study by OPTS. However, a very large number of other plasticizers remain that are not under study, and little information has been compiled on these materials. Three classes of plasticizers were selected for investigation during this task. These were:

* Epoxy compounds derived from soybean oil, linseed oil, or tall oil;

* Linear polyesters derived from adipic, sebacic, phthalic or glutaric acids;

* Trimellitic acid esters (trimellitates).

The objectives of this study were to compile and analyze published information for each individual plasticizer in the areas of physical and chemical data, potential occupational and environmental exposure, manufacturing sites and processes, use patterns, environmental degradation, biological effects, and plasticizer interchangeability.

This report is divided into eight major sections. Section I presents a brief introduction to the report and outlines the overall program objectives. Section II contains the summary. Section III outlines the methodology and data acquisition techniques employed in the study. Section IV presents the physical and chemical properties. Section V describes the manufacturing and use information. Section VI provides data on environmental and health effects. Section VII contains information on plasticizer interchangeability.

SECTION II

SUMMARY

Epoxide derivatives of soybean oil, linseed oil, and tall oil esters; linear polyesters; and esters of trimellitic acid are three classes of plasticizers employed in a variety of plastics (primarily polyvinyl chloride) and elastomers. Small quantities are used in various coating applications. In general, the three classes of plasticizers impart good high or low temperature flexibility while exhibiting low volatility, low migration rates, and good resistance to oil or water extraction from the plastic medium.

In 1979, production volumes of these plasticizers were stated to be: 130 million pounds for epoxy plasticizers; 55 million pounds for linear polyesters; and 31 million pounds for trimellitates. For epoxy compounds, production processes use either performic acid or peracetic acid. With linear polyesters and trimellitates, multipurpose equipment is used in the production of esters from the corresponding acids and alcohols.

Little published information is available concerning the health effects of any of the three classes of plasticizers. No occupational standards exist for any of the three classes. Feeding studies using rats and dogs showed no significant toxic effects for epoxy compounds at levels up to 5% in the diet. Skin and eye irritation tests showed epoxy compounds to be either mild irritants or to be nonirritants. Two-year chronic feeding studies with a linear polyester using rats and dogs showed no significant toxic effects at levels up to 1% in the diet. Skin and eye tests generally showed little or no irritation. For trimellitates, no studies were found in the literature; data were obtained from manufacturers. Acute oral LD_{50} studies with rats, mice, and rabbits showed these compounds to have relatively low toxicity. In one inhalation study, during which the trimellitate was heated to 180°C, rats exposed to the vapor died. These deaths were delayed for up to 3 days after conclusion of the tests.

Environmental tests were limited to static fish toxicity studies for two trimellitates and studies of fungal and bacterial growth on epoxy compounds and linear polyesters. In the fish toxicity studies, the 96-hr tests showed the trimellitates to be nontoxic towards fingerling rainbow trout and bluegill. Numerous studies of plasticizer degradation were reported for fungal and bacterial action on epoxy compounds and linear polyesters. The results of all studies showed both classes of plasticizers to be very susceptible to attack.

SECTION III

METHODOLOGY AND DATA SOURCES

This section describes the methodology used and identifies the data sources employed for the acquisition of information presented in the report.

LITERATURE SOURCES

A number of books and periodicals were investigated as potential sources of information concerning the manufacture and use of the various classes of plasticizers. Among the sources employed were the following books and periodicals:

* Encyclopedia of Chemical Technology;
* Encyclopedia of Polymer Science and Technology;
* Chemical and Process Technology Encyclopedia;
* Encyclopedia of PVC;
* Chemical Process Industries;
* Industrial Chemicals;
* Directory of Chemical Producers;
* Chemical Economics Handbook;
* Various trade publications such as Modern Plastics, Plastics Technology, Chemical Marketing Reporter, Modern Plastics Encyclopedia; and
* Government publications.

COMPUTER DATA SYSTEMS

Searches were made of various computer-based data storage systems for information on each class of plasticizer and on each of the specific plasticizers known to be in commercial production. For most searches, the Chemical Abstracts Service Registry Number was employed as the initial code. For those systems that did not employ the registry numbers, the full names of the specific plasticizers, as denoted in the TSCA Candidate List of Chemical Substances, were employed. Brief synopses of the various data storage systems used for the search and the source of the data file are presented alphabetically in the following subsections.

BIOSIS Previews

This file contains citations from both Biological Abstracts and Bioresearch Index, the major publications of Biosciences Information Service of Biological Abstracts. Together, these publications constitute the major English language service providing comprehensive worldwide coverage of research in the life sciences. Approximately 8,000 primary journals as well as reviews, preliminary reports, selected institutional and government reports, and research communications are included for all aspects of the biosciences and medical research. The file is divided into two separate sections, one covering 1969 through 1971 and the other from 1971 to present. Approximately 2,300,000 records are included in this data source of Biosciences Information Service, Philadelphia, Pennsylvania.

Chemical Abstracts (CA) Search

The CA Search is an expanded data source which resulted from the merger of two files: the CA Condensates file and the CASIA file. The CA Condensates file contains the basic bibliographic information appearing in the printed Chemical Abstracts volumes. The CASIA file contains the general subject headings from a controlled vocabulary and the CAS Registry Numbers. Other uncontrolled vocabulary terms and cross-referenced general subject headings are also included. This data source is divided into three files: 1967-1971; 1972-1976; and 1977-present. Approximately 4,000,000 records are included in this data source from Chemical Abstracts Service, Columbus, Ohio.

Enviroline

This data file covers environmental information including management, technology, planning, law, political science, economics, geology, biology, and chemistry as they relate to environmental issues. The interdisciplinary approach provides indexing and abstracting coverage of more than 5,000 international primary and secondary source publications including periodicals, government documents, industry reports, monographs, proceedings of meetings, and rulings from the Federal Register. This file covers 1971 to the present and contains about 75,000 citations. It is a product of the Environment Information Center, Inc., New York.

Environmental Periodicals Bibliography (EPB)

The EPB data file covers the fields of general human ecology, atmospheric studies, energy, land and water resources, and nutrition and health. Approximately 250 periodicals are indexed for this data source. This file covers 1973 to the present and contains about 137,000 records. It is a product of the Environmental Studies Institute, Santa Barbara, California.

Excerpta Medica

This data source is one of the major sources for searching the biomedical literature. It consists of abstracts and citations of articles from over 3,500 biomedical journals published throughout the world. The file covers the entire field of human medicine and related disciplines. An online file corresponds to the 43 separate specialty abstract journals and 2 literature indexes. This data source covers June 1974 to the present and contains in excess of 1,003,000 records. It is available through Excerpta Medica, Amsterdam, The Netherlands.

Medline

This data source is a service of the National Library of Medicine in Bethesda, Maryland. It contains approximately 600,000 references to biomedical journal articles published in the current and two preceding years. The articles are from 3,000 journals published in the U.S. and 70 foreign countries as well as a limited number of chapters and articles from selected monographs. In addition to the current file from 1978 to are present, back files are available to cover 1966-1968, 1969-1971, 1972-1974, 1975, and 1976-1977. Total references in all files exceed 2,250,000.

National Technical Information Service (NTIS)

The NTIS data base consists of government sponsored research, development, and engineering plus analyses prepared by federal agencies and their contractors or grantees. It provides a means through which unclassified, publicly available, unlimited distribution reports are made available from governmental agencies. The data base includes material from both the hard and soft sciences, including many topics of broad interest such as environmental pollution and control, energy conversion, technology transfer, behavioral/societal problems, and urban and regional planning. This data source covers 1964 to the present and contains about 730,000 citations. The file is a product of NTIS, U.S. Department of Commerce, Springfield, Virginia.

Pollution Abstracts

This data source is one of the primary resources for references to environment-related literature on pollution, its sources, and its control. The file covers subjects such as air pollution, environmental quality, noise pollution, pesticides, radiation, solid waste, and water pollution. This source covers 1970 to the present and currently contains about 67,000 citations. It is a product of Data Courier, Inc., Louisville, Kentucky.

RAPRA Abstracts

The Rubber and Plastics Association (RAPRA) data file is a comprehensive source covering the commercial, technical, and research aspects of the rubber and plastics industries. It provides information on materials including synthesis and polymerization, raw materials and monomers, and compounding

ingredients. RAPRA includes information on applications of polymers, toxicity reports, and potential environmental and industrial health hazards. This data source covers 1972 to the present and contains approximately 110,000 records. It is maintained by the Rubber and Plastics Research Association of Great Britain, Shawbury, Shrewsbury, Shropshire, England.

Science Citation Index (SCISEARCH®)

This data source is a multidisciplinary index to the literature of science and technology and includes all records published in Science Citation Index (SCI®) and additional records from the Current Contents series of publications that are not included in the printed version of SCI. The file contains reference from about 2,600 major scientific and technical journals and covers all areas of the pure and applied sciences. This source covers 1974 to the present in two files; one file covers 1974-1977 and the other, 1978 to the present. Total citations from both files number about 2,700,000. The data file is produced by the Institute for Scientific Information, Philadelphia, Pennsylvania.

SSIE Current Research

The Smithsonian Science Information Exchange (SSIE) Current Research is a data file containing reports of both government and privately funded scientific research projects, either currently in progress or initiated and completed during the most recent two years. Data are collected from the funding organization at the inception of a research project in all fields of basic and applied research in the life, physical, social, and engineering sciences. Project descriptions are received from over 1,300 organizations that fund research, including federal, state, and local government agencies; nonprofit associations and foundations; and colleges and universities. About 90% of the information in the data base is provided by agencies of the federal government. The most recent data file (1978-present) contains in excess of 250,000 citations. This source is maintained by the Smithsonian Science Information Exchange, Washington, D.C.

Toxicology Data Bank (TDB)

This data source contains chemical, pharmacological, and toxicological information and data on approximately 1,000 compounds. Information is being prepared on an additional 1,500 compounds. Data for this file are extracted from handbooks and textbooks and subject to review by a peer group of subject specialists. This source is a service of the National Library of Medicine, Bethesda, Maryland.

Toxline

The Toxicology Information Online source is a service of the National Library of Medicine in Bethesda, Maryland. This source is a collection of over 520,000 references from the last five years of published work on human and animal toxicity studies, effects of environmental chemicals and pollutants, and adverse drug reactions. Essentially all references have abstracts

or indexing terms, and most compounds are identified by the CAS Registry Numbers. The references employed in this source are from five major published secondary sources and five special literature collections maintained by other organizations. The current file covers 1974 to the present. Older material (~ 400,000 references) is contained in a separate file designated Toxback.

OTHER SOURCES

Telephone and letter contacts were made with industry trade organizations, manufacturers, distributors, and users to identify and collect available information relating to the various classes of plasticizers. Information was obtained on the physical and chemical properties of many of the specific plasticizers of interest. In addition, information was obtained relating to the manufacturing process, product purity, product losses, use patterns, environmental effects, and health effects for each class of plasticizer. Except for environmental effects and health effects, little information can be found in the published literature for the other topics. The information provided by the groups identified above was the sole source of the data.

SECTION IV

PHYSICAL AND CHEMICAL PROPERTIES

This section presents discussion of the characterization of each class of plasticizer, a compilation of the physical properties of the commercial products, and a discussion of the chemical properties of each class.

EPOXY COMPOUNDS

This subsection will provide a discussion of the nature of the raw materials as well as a discussion of the physical and chemical properties of the epoxy compounds.

Characterization

Soybean Oil--

Soybean oil is a triglyceride comprised of glycerol and several unsaturated fatty acids. It is extracted from the crushed bean with a mixture of petroleum hydrocarbons. The oil is further refined with sodium hydroxide or sodium carbonate to remove excess fatty acids, and then the oil is bleached. The chemical structure of this oil is quite complex owing to the combinations and permutations of fatty acids that can be esterified at the three nonequivalent (enzymatically) hydroxyl groups of the glycerol. A generalized triglyceride has the following structure, without regard for optical activity:

R = fatty acid component

Soybean oil has the following composition with respect to the fatty acid components of the triglyceride (Applewhite, 1980):

Acid	Structure	% Composition
Hexadecanoic (palmitic)	$CH_3(CH_2)_{14}CO_2H$	2.3-10.6
Octadecanoic (stearic)	$CH_3(CH_2)_{16}CO_2H$	2 4-6
cis-9-Octadecenoic (oleic)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	23.5-30.8

cis,cis-9,12-Octadecadienoic (linoleic) $CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7CO_2H$ 49-51.5

cis,cis,cis-9,12,15-Octadecatrienoic (linolenic) $CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H$ 2-10.5

Linseed Oil--

Like soybean oil, linseed oil is also a triglyceride derived from glycerol and unsaturated fatty acids. It is produced from the seeds of the common flax plant; the seeds contain approximately 33-43% oil (Conan, 1980). Climatic conditions at the time the oil is developed in the seed affect the degree of unsaturation; the lower the temperature, the higher the extent of unsaturation. The flaxseed is normally reduced to 20-30% oil in a screw press, and then the residual oil is extracted from the crushed seed with hexane. Further treatment of the crude oil is usually the same as described for soybean oil.

Linseed oil contains the same fatty acids as soybean oil but exhibits a somewhat higher degree of unsaturation. The typical composition of linseed oil and a comparison to soybean oil are as follows (Cowan, 1980):

Acid	% Composition (linseed oil)	% Composition (soybean oil)
Hexadecanoic	6	~ 2-11
Octadecanoic	4	~ 2-6
cis-9-Octadecenoic	13-37	~ 24-31
cis,cis-9,12-Octadecadienoic	5-23	~ 49-52
cis,cis,cis-9,12,15-Octadecatrienoic	26-58	~ 2-11

Tall Oil--

Tall oil is the major by-product of the kraft or sulfate pulping process; it is a mixture of resin, fatty acids, and unsaponifiables. The crude oil is obtained by the acidification of the resin and fatty acid sodium soaps recovered from the concentrated black liquor resulting from the pulping process. Crude oil derived from pine trees in the various regions of the U.S. contains approximately 43-56% fatty acids, 39-51% rosin acids, and 5-7% unsaponifiables (Tate, 1969).

Many refining methods have been developed for the separation of the rosin acids and the tall oil fatty acids. These methods include physical and chemical techniques, as well as combinations of both techniques. Most of the components in crude tall oil are decomposed or transformed when subjected to high temperatures so that distillations are usually performed under high vacuum using superheated steam. This simple distillation procedure is normally followed by fractional distillation to obtain a mixture of refined tall oil fatty acids (Johnson, 1978). A typical composition of tall oil fatty acids in a refined, low-rosin mixture is as follows:

Acid	% Composition
Hexadecanoic (palmitic)	1
Octadecanoic (stearic)	2
cis-9-Octadecenoic (oleic)	48-51
cis,cis-9,12-Octadecadienoic (linoleic, nonconjugated)	37-40
cis,cis-10,12-Octadecadienoic (linoleic, conjugated)	5
Unknown	4

The percentage composition data are basically from the literature (Tate, 1969) but modified slightly by MRI to normalize the percentage.

Prior to formation of the corresponding epoxy compounds, the tall oil acids are treated with C_4 or higher alcohols, such as 2-ethylhexanol, n-octyl alcohol, or n-butyl alcohol, to form the corresponding esters.

Epoxidation--

Each of the three classes of oils (or esters of the acids) are epoxidized by a variety of methods depending upon the specific manufacturer or the desired properties of the resultant product. The production processes for the formation of the epoxy compounds from these raw materials are discussed in detail in Section V.

Physical Properties

Each manufacturer of epoxy compounds was contacted for information relating to the physical properties of their respective compounds. The results are compiled in Table IV-1. Generally, the test procedures were not identified by the manufacturers. If identified, the procedures were either American Society for Testing and Materials (ASTM, 1980) or American Oil Chemists Society (AOCS, 1974) methods. No data were available for properties such as vapor pressure, solubility in water or organic solvents, or octanol-water coefficients that would provide some insight into the potential for environmental transport. Chemical Abstracts numbers and synopses of selected physical properties are provided in the following subsections.

Chemical Abstracts Service Registry Numbers--

Chemical Abstracts numbers (CAS numbers, CASRN) for the epoxy compounds of interest to this study are as follows:

Compound	CAS number
Epoxidized soybean oil	8013-07-8
Epoxidized soya oil	61788-96-3
Epoxidized linseed oil	8016-11-3
Epoxidized linseed oil, butyl ester	68991-46-8
Octyl epoxytallate	61788-72-5
2-Ethylhexyl epoxytallates	61789-01-3

TABLE IV-1. PHYSICAL PROPERTIES OF COMMERCIAL EPOXY COMPOUNDS

Compound	Approximate molecular weight	Specific gravity	Viscosity (cps at 25°C)[a]	Refractive index (25°C)	Oxirane oxygen (%)	Iodine number	Acid number (mg KOH/g)	Saponification number	Solubility: In water (% by wt.)	Solubility: Water in (% by wt.)	Freezing point (°C)	Pour point[b] (°C)	Flash point (°C)[c]
Epoxidized soybean oil													
Polycizer ESO[d]	1000	0.993 (25/20°C)	372	1.4730 (20°C)	7.3	0.8	0.4	NA[e]	NA	NA	NA	-2	316
Flexol EPO[f]	1000	0.9977 (20/20°C)	518 (20°C)	NA	7.0	NA	NA	NA	<0.01 (25°C)	0.55 (25°C)	NA	-2	157
E.S.O.[g]	1000	0.995 (25/25°C)	340	1.472	6.9	1.5	0.5	183-185	NA	NA	NA	-10 to -5	316
Nuoplaz 849[h]	1000	0.99 (25/25°C)	320	1.4565	NA	NA	0.47	NA	NA	NA	NA	0	288
Plastolein 9232[i]	NA	0.99 (20/20°C)	159	1.470	6.5	2.5	1.0	NA	NA	NA	-18	NA	307
Drapex 6.8[j]	1000	0.992 (25/25°C)	320	1.4720	7.25	1.3	0.5	NA	<0.01 (20°C)	NA	NA	0	143
Epoxol 7-4[k]	NA	0.994 (25/25°C)	314	1.4705	7.4	NA	0.10	178.1	NA	NA	NA	-4	310
Vikoflex 7170[l]	1000	0.992 (25/25°C)	317-416	1.472	7.0.7.2	NA	0.3	NA	NA	NA	0	NA	NA
Peroxidol 780[m]	1000	0.991 (23/15.5°C)	355	1.4720 (23°C)	7.3	NA	0.33	NA	NA	NA	NA	-2	316
Admex 710 & 711[n]	NA	0.994 (25/25°C)	368	1.471	NA	NA	0.3	NA	NA	NA	NA	-4 to 2	310
Paraplex G-60[o]	1000	0.980 (25/15°C)	350	1.472	NA	NA	0.6	182	NA	NA	5	NA	310
Paraplex G-62[o]	1000	0.993 (25/15°C)	550	1.471	NA	NA	0.4	183	NA	NA	5	NA	310
Plas-Chek 775[p]	1000	0.998 (25/25°C)	875	1.472	7.3	1.5	0.5	NA	NA	NA	NA	-4	316
Epoxidized linseed oil													
Flexol LOE[f]	1000	1.030 (25/20°C)	700 (20°C)	NA	9.0	NA	NA	NA	<0.015 (25°C)	0.017 (25°C)	NA	-3	238
Drapex 10.4[j]	1000	1.0385 (25/25°C)	1000	1.4788	9.6	2.0	0.5	NA	<0.01 (20°C)	NA	NA	-5	290
Epoxol 9-5[k]	NA	1.030 (25/25°C)	619	1.4715	9.2	NA	0.12	172	NA	NA	NA	-1	313

continued

TABLE IV-1. (continued)

Compound	Approximate molecular weight	Specific gravity	Viscosity (cps at 25°C)[a]	Refractive index (25°C)	Oxirane oxygen (%)	Iodine number	Acid number (mg KOH/g)	Saponification number	Solubility: In water (% by wt.)	Solubility: Water in (% by wt.)	Freezing point (°C)	Pour[b] point (°C)	Flash point (°C)[c]
Plas-Chek 795[p]	NA	1.03 (25/25°C)	399	1.477	9.4	NA	0.3	NA	NA	NA	NA	NA	310
Admex ELO[n]	NA	1.032 (25/25°C)	815	1.477	NA	NA	1.0	NA	NA	NA	NA	-1	310
Octyl esters of tall oil fatty acids													
Nuoplaz 850[h]	420	0.92 (25/25°C)	20	1.4565	NA	NA	0.75	NA	NA	NA	NA	-22	221
Peroxidol 781[m]	424	0.924 (23/15.5°C)	46.6	1.4580 (23°C)	4.9	NA	0.5	NA	NA	NA	NA	-15	235
Drapex 4.4[j]	420	0.992 (25/25°C)	20	1.4580	5.1	2.2	0.5	NA	<0.01 (20°C)	NA	-20	NA	220
Flexol EP-8(o)[f]	420	0.9232 (20/20°C)	35.2 (20°C)	NA	4.7	NA	NA	NA	<0.01 (20°C)	0.3 (20°C)	NA	-8.5	193
Plastolein 9215[k]	NA	0.82 (20/20°C)	62	1.463	4.2	4.0	2.0	NA	NA	NA	-7	NA	282

a cps = centipoise: $\frac{gm}{sec \times cm}$ x 100; at 20°C, the viscosity of water ≡ 1.0 cps.
b Test method was ASTM D 97-66.
c Most test methods were Cleveland Open Cup. Others did not list the specific method used. Test method was ASTM D 92-66.
d Harwicke Chemical Corporation.
e NA - Not Available.
f Union Carbide Company.
g FMC Corporation.
h Tenneco Chemicals.
i Emery Industries.
j Argus Chemical Corporation, a subsidiary of Witco Chemical Corporation.
k Swift Specialty Chemicals.
l Viking Chemical Company.
m Reichold Chemicals.
n Sherex Chemicals.
o Rohm & Haas Company.
p Ferro Corporation.

Other epoxy compounds are listed in compilations such as the Toxic Substances Control Act (TSCA) Candidate List of Chemical Substances but are not among the products in Table IV-1 for which data were supplied by producers or distributors. Many reasons could account for these omissions, including discontinued products, uses other than as plasticizers, captive uses, special orders, and low volume specialty items.

Specific Gravity--

For epoxidized soybean oils, the specific gravity of essentially all of the listed commercial products is in the range of 0.991 to 0.998. With epoxidized linseed oil, all values except one were in the range of 1.030 to 1.039. Three of the four octyl tallates had values between 0.920 and 0.924. Overall, the epoxidized linseed oils had the highest specific gravity, followed by the epoxidized soybean oils; the octyl epoxytallates had the lowest values. Identified test method was ASTM D 1298-67.

Viscosity--

The viscosity of the various epoxidized soybean oils showed a wide variance, ranging from about 60 to 875 centipoise. Epoxidized linseed oils also showed a wide range of viscosity levels, ranging from about 400 to 1,000. For the four octyl epoxytallates, the levels were considerably lower and more uniform with the range being 20 to 47 centipoise. Identified test methods were ASTM D 445-65 or ASTM D 2393-68.

Oxirane Content--

Oxirane content is the percentage of oxygen incorporated in the material during epoxidation that is present as the oxygen in the oxirane structure, a three-membered ring containing one oxygen and two carbon atoms. The percentage oxirane content for almost all of the epoxidized soybean oils ranges from about 6.9 to 7.4%. Epoxidized linseed oils show a greater percentage of oxirane content because of the greater degree of unsaturation in the raw material triglyceride. Percentage levels for all but one linseed oil range from 9.0 to 9.6%. Octyl epoxytallates show the lowest oxirane content with levels from 4.7 to 5.1%. Identified test method was AOCS Cd 9-57.

Iodine Number--

The iodine number represents the grams of iodine absorbed per 100 grams of epoxidized material. This number is a measure of the unsaturation remaining after the epoxidation process. Since the oxirane content measures unsaturation lost to oxirane formation, these values and the iodine number should show an inverse relationship. For essentially all epoxidized soybean oils listed in the table, the iodine numbers are about 0.8 to 1.5. Iodine numbers were given for only two epoxidized linseed oils and one octyl epoxytallate. Published test method was AOCS Tg-1-64.

Acid Number--

Acid number or value is the quantity of base (e.g. potassium hydroxide) required to neutralize the free fatty acid in one gram of epoxidized product. For the epoxidized soybean oils, the values ranged from 0.1 to 0.6 mg except for two products which showed values of 1.0 and 2.0 mg. These two products are also the same ones with low oxirane oxygen content and high iodine number.

This indicates that quantities of free unsaturated acid are likely present in these two products. Acid numbers for the epoxidized linseed oils ranged from about 0.1 to 1.0 mg; those for octyl epoxytallates ranged from 0.5 to 0.75 mg. Identified test methods were ASTM D 1045-80 and AOCS Te-2a-64.

Saponification Number-

The saponification number is the quantity of base required to saponify the esters and acids in one gram of plasticizer. Very few numbers were provided for any of the epoxy plasticizers, but the values that were reported ranged from 150 to 185. Test methods were not identified.

Solubility--

Very few data were reported for the epoxy plasticizers. In general, the solubilities in water are quite low, usually in the range of 0.01% by weight or less. This very low solubility may account for the few data reported. The test methods employed were not identified.

Chemical Properties

No studies were found in the literature related to the chemical properties of the epoxy plasticizers in the pure state; however, considerable work has been performed on these plasticizers as components of an overall polymer system. Most testing has been done on plastic films or sheets which contain the plasticizer as part of the system.

As would be expected, most of the studies are concerned with the changes in the polymer properties rather than information on the components. It is known that the epoxides in a polymer system undergo photooxidation near the polymer surface and that these photooxidation products will not migrate back into the film. The products remain on the film surface and form a crusty layer. No information is available on the nature of the specific oxidation products. The only apparent concern is how these products will affect the properties and utility of the film.

Information from manufacturers of epoxy compounds shows that these materials react in much the same manner as would be expected for compounds containing an epoxide group. Lewis acids react readily with the epoxide group resulting in ring opening and polymerization. If polymerization does occur, information from manufacturers states that the incidence of a hazardous reaction is rare. If cross-linking of the epoxy compound is desired, Lewis acids are common agents for this purpose.

Since triglycerides (i.e. soybean oil and linseed oil) are esters, the oils are susceptible to acid or base hydrolysis. Acid hydrolysis occurs rapidly at room temperature. Base hydrolysis, as used for saponification measurements, occurs readily at approximately 70°C at a pH of about 8. No rate data on these hydrolysis reactions were available in the published literature or from manufacturers.

LINEAR POLYESTERS

This subsection will present a discussion of the nature of the raw materials and a discussion of the physical and chemical properties of these plasticizers.

Characterization

Polyester plasticizers are high molecular weight polymers derived from a dibasic acid and a glycol. The reaction is terminated using either a long-chain alcohol or a fatty acid in the C_{12}-C_{18} range. This relation can be shown schematically as follows:

$$x\,[HO_2C\text{-}A\text{-}CO_2H] + x[HO\text{-}G\text{-}OH] \longrightarrow \left(\text{-C(=O)-A-C(=O)-O-G-O-}\right)_x + 2H_2O$$

$$\left(\text{-C(=O)-A-C(=O)-O-G-O-}\right)_x + 2\ ROH \longrightarrow R\text{-}O\left(\text{-C(=O)-A-C(=O)-O-G-O-}\right)_x\text{C(=O)-A-C(=O)-R}$$

alcohol terminated

$$\left(\text{-C(=O)-A-C(=O)-O-G-O-}\right)_x + 2\ RCOH \longrightarrow RC(=O)\left(\text{-O-G-O-C(=O)-A-C(=O)-}\right)_x\text{O-G-O-C(=O)R}$$

acid terminated

where A is the dibasic acid, G is the glycol, and T is the terminating alcohol or acid. Most polyester plasticizers are tailored to function in specific roles and to have specific physical properties or combination of properties. Because they are designed for specific purposes, it is very difficult to precisely characterize each of these plasticizers.

Current polyesters generally employ adipic acid, sebacic acid, or azelaic acid as the dibasic acid. It is believed that some manufacturers use phthalic anhydride to lower the cost of the polyesters and improve compatibility but at a sacrifice in plasticizer efficiency. Propylene glycol, trimethylene glycol, or butylene glycol are generally employed as the glycols. Ethylene glycol is seldom used because it produces a solid product. The terminating acids or alcohols can be isodecyl alcohol, 2-ethylhexanol, stearic acid, oleic acid, or other alcohols or acids which will produce the desired properties in the polyester. The structures of the more common acids and glycols are as follows:

Dibasic acid	
Adipic	$HO_2C(CH_2)_4CO_2H$
Azelaic	$HO_2C(CH_2)_7CO_2H$
Sebacic	$HO_2C(CH_2)_8CO_2H$

Glycol	
1,2-Propanediol	$HOCH_2CHOHCH_3$
1,3-Propanediol	$HOCH_2CH_2CH_2OH$
1,3-Butanediol	$HOCH_2CH_2CHOHCH_3$
1,4-Butanediol	$HOCH_2CH_2CH_2CH_2OH$

Approximate molecular weights of the polyester plasticizers generally range from 2,000 to 3,000, but some are as low as about 800 and as high as 8,000.

Physical Properties

Each manufacturer of linear polyesters was contacted for information relating to the physical properties of their respective products. These data are compiled in Table IV-2. Generally the test procedures were not identified by the manufacturer. If identified, the procedures were either ASTM or AOCS methods. No data were available for properties such as vapor pressure, solubility in water or organic solvents, octanol-water coefficients, or others that would provide some insight into the potential for environmental transport. Chemical Abstracts numbers of the more commercially significant polyesters and synopses of selected physical properties are presented in the following subsections.

Chemical Abstracts Service Registry Numbers--

Chemical Abstracts numbers (CAS numbers, CASRN) for those polyesters which have commercial significance are presented in Table IV-3. Many other polyesters are listed in compilations such as the TSCA Candidate List of Chemical Substances but are not employed to any significant extent as plasticizers in plastics. It is estimated by MRI that the materials listed in Table IV-3 comprise approximately 90% of the total quantity of polyesters currently used as plasticizers in plastics.

Specific Gravity--

The specific gravity for most of the linear polyesters generally is within the range of 1.0 to 1.1. This indicates that the majority of these plasticizers have approximately the same bulk weight as water. Published test method was ASTM D 2111-71.

Viscosity--

The viscosity of the various linear polyesters shows a wide variance, ranging from about 130 to 220,000 centipoise. This wide range is expected because of the variety of molecular weights and the different chemical entities comprising each of the materials. Identified test method was ASTM D 1638-74.

Acid Number--

As defined earlier in this section, the acid number is a measure of the free acid functionalities present in the material. For the polyesters, the acid numbers generally range from ~ 0.5 to 4.0. Some commercial products show relatively high acid numbers (20-30) indicating large quantities of free acid groups within the polymer. Published test method was AOCS Cd 3a-63.

Saponification Number--

The saponification number is a measure of the quantity of ester and acids present in the product. Relatively few numbers were available for the polyesters. Those values which were reported generally range from 400 to 600. Identified test method was AOCS Cd 3-25.

TABLE IV-2. PHYSICAL PROPERTIES OF LINEAR POLYESTER PLASTICIZERS

	Approximate molecular weight	Specific gravity (25/25°C)	Refractive index (25°C)	Viscosity (cps at 25°C)[a]	Acid number (mg KOH/g)	Saponification number	Freezing point (°C)	Pour point (°C)	Flash point (°C; COC)[b]	Fire point (°C; COC)[b]	Color APHA[c]	Color Gardner[d]
Nuoplaz[e] 6186	NA[f]	1.05-1.07	1.4640	434	2.0	NA	NA	-32	266	NA	70	NA
Nuoplaz 6187	NA	1.085-1.095	1.4670	2,317	2.0	NA	NA	-18	277	NA	70	NA
Nuoplaz 6188	NA	1.0-1.03	1.4735	139	2.0	NA	NA	-34	231	NA	70	NA
Morflex[g] P-50	3,000	1.125±0.1[h]	1.4709	12,353	NA	NA	NA	2	288	NA	500	NA
Morflex P-50A	3,000	1.124±0.1[h]	1.4695	11,343	NA	NA	NA	7	285	NA	500	NA
Morflex P-51A	2,000	1.116±0.01[h]	1.4660	4,950	NA	NA	NA	-9	277	NA	600	NA
Plastolein[i] 9717	NA	1.02	1.469	260	2.5	NA	18	NA	232	NA	NA	5
Plastolein 9720	NA	1.03	1.462	213	3.0	NA	18	NA	260	NA	NA	5
Plastolein 9730	NA	1.06	1.483	943	3.0	NA	45	NA	266	NA	NA	6
Plastolein 9731	NA	1.06	1.483	933	3.0	NA	45	NA	266	NA	NA	6
Plastolein 9734	NA	1.04	1.483	1,681	3.0	NA	55	NA	260	NA	NA	6
Plastolein 9746	NA	NA	NA	NA	2.5	NA	NA	NA	237	NA	NA	5
Plastolein 9750	NA	1.06	1.477	908	3.0	NA	32	NA	279	NA	NA	5
Plastolein 9761	NA	1.06	1.469	2,062	3.0	NA	10	NA	268	NA	NA	2
Plastolein 9765	NA	1.08	1.479	3,224	3.0	NA	35	NA	277	NA	NA	6
Plastolein 9772	NA	1.04	1.486	390	3.0	NA	16	NA	271	NA	NA	3
Plastolein 9775	NA	1.08	1.465	1,415	3.0	NA	52	NA	299	NA	NA	20.0
Plastolein 9776	NA	1.08	1.466	2,778	2.0	NA	-4	NA	302	NA	NA	2
Plastolein 9780	NA	1.04	1.466	1,071	3.0	NA	-2	NA	299	NA	NA	7
Plastolein 9783	NA	1.08	1.465	1,211	2.0	NA	55	NA	282	NA	NA	5

continued

TABLE IV-2. (continued)

	Approximate molecular weight	Specific gravity (25/25°C)	Refractive index (25°C)	Viscosity (cps at 25°C)[a]	Acid number (mg KOH/g)	Saponification number	Freezing point (°C)	Pour point (°C)	Flash point (°C; COC)[b]	Fire point (°C; COC)[b]	Color APHA[c]	Color Gardner[d]
Plastolein 9789	NA	1.08	1.460	17,280	5.0	NA	-20	NA	304	NA	NA	4
Plastolein 9790	NA	1.08	1.46	17,280	5.0	NA	-20	NA	304	NA	NA	7
Ultramoll[j] I	NA	1.075-1.090[k]	1.472	2,000-3,000	≦ 1.0	490-510	NA	NA	280-300	NA	NA	NA
Ultramoll II	NA	1.100-1.115[k]	1.472	2,000-3,000	≦ 1.0	510-540	≦ -10	NA	280-300	NA	NA	NA
Ultramoll III	NA	1.100-1.110[k]	1.469	1,000-1,300	≦ 1.0	510-530	≦ -20	NA	270-290	NA	NA	NA
Ultramoll PP	NA	1.035-1.045[k]	1.502	1,200-1,500	≦ 0.5	300-320	≦ -35	NA	230-265	NA	NA	NA
Ultramoll TGN	NA	1.090-1.100[k]	1.503	2,000-2,500	≦ 1.0	300-320	≦ -20	NA	220-240	NA	NA	NA
Hercoflex[l] 900	NA	1.22	NA	NA	20-30	NA	NA	NA	238	NA	NA	6
Santicizer[m] 412	NA	1.030-1.060	1.453-1.463	240-250	NA	NA	NA	-20	257	282	250	NA
Santicizer 429	NA	1.080-1.110	1.460-1.470	4,300-6,700	NA	NA	NA	-18	288	310	250	NA
Santicizer 334F	2,000	1.080-1.084	1.4654	3,100-3,800	NA	NA	NA	3	277	299	100[n]	NA
Santicizer 409	NA	1.080-1.084	1.4654	3,100-3,800	NA	NA	NA	4	277	299	100[n]	NA
Santicizer 411	NA	1.104-1.110	1.4772	7,900-9,800	NA	NA	NA	21.1	282	NA	100[n]	NA
Staflex[o] RS-550	2,500	1.069[p]	1.4658(23°C)	2,850	2.8	NA	NA	-12	280	NA	75	NA
Staflex RS-802	1,900	1.087[p]	1.4819(23°C)	4,450	1.96	NA	NA	-15	250	NA	80	NA
Staflex RS-804	1,900	1.075[p]	1.4743(23°C)	2,600	2.2	NA	NA	-15	260	NA	75	NA
Staflex RS-809	2,100	1.079[p]	1.4760(23°C)	4,800	2.2	NA	NA	-12	260	NA	80	NA
Resoflex[q] R-296	NA	NA	1.471	NA	32	NA	NA	NA	NA	NA	NA	3
Resoflex R-446	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Resoflex R-460	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Resoflex R-804	NA	NA	NA	NA	25	NA	NA	NA	NA	NA	NA	4

continued

TABLE IV-2. (continued)

	Approximate molecular weight	Specific gravity (25/25°C)	Refractive index (25°C)	Viscosity (cps at 25°C)[a]	Acid number (mg KOH/g)	Saponification number	Freezing point (°C)	Pour point (°C)	Flash point (°C; COC)[b]	Fire point (°C; COC)[b]	Color APHA[c]	Color Gardner[d]
Resoflex R-766	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Plasthall® HA7A	NA	1.53	1.4662	NA	3.0	585-592	NA	NA	270	310	NA	NA
Plasthall P-630	NA	1.08	1.464	2,350	0.4	519	-18	NA	268	304	NA	2-3
Plasthall P-640	NA	1.09	1.466	5,800	0.4	517	-22	NA	274	318	NA	< 1
Plasthall P-644	NA	1.11	1.469	76,000	1.0	548	-28	NA	288	327	NA	< 1
Plasthall P-7035	4,500	1.07	NA	11,300	NA	510	-12	NA	260+	260+	NA	4
Plasthall P-7092	NA	1.11	NA	24,000	NA	NA	-20[s]	NA	271	316	NA	8-9
Plasthall MX-1202	NA	0.957	1.467	550	1.3	257	-32	NA	172	198	NA	NA
Plasthall P-530	NA	1.10	1.464	2,250	0.3	559	-15	NA	304	316	NA	3-4
Plasthall P-540	NA	1.11	1.466	5,750	1.5	558	-22	NA	271	310	NA	2-3
Plasthall P-550	NA	1.05	1.463	2,850	0.7	474	-41	NA	279	332	NA	2-3
Plasthall P-643	NA	1.074	1.4649	2,650	0.5	486	-5	NA	282	316	NA	< 1
Plasthall P-1070	NA	1.068-1.076	NA	5,000	2.0	455	-22	NA	218	249	NA	3-4
Plasthall P-7046	NA	1.105	NA	11,000	0.9	317	< -25	NA	266	310	NA	4-5
Plasthall MX-502	NA	0.995	1.4641	420	NA	NA	-25	NA	182	196	NA	NA
Admex® 433	NA	1.090	1.5050	1,900	2.0	NA	NA	-8	235	260	NA	3
Admex 515	NA	1.050	1.4630	575	2.5	NA	NA	2	246	291	150	NA
Admex 522	NA	1.060	1.5040	795	2.0	NA	NA	-21	241	260	NA	3
Admex 523	NA	1.100	1.5140	3,960	2.0	NA	NA	-7	232	254	NA	3
Admex 525	NA	1.035	1.4609	310	3.0	NA	NA	-34	274	291	NA	1
Admex 529	NA	1.122	1.4695	4,150	3.0	NA	NA	0	280	306	NA	2

continued

TABLE IV-2. (continued)

	Approximate molecular weight	Specific gravity (25/25°C)	Refractive index (25°C)	Viscosity (cps at 25°C)[a]	Acid number (mg KOH/g)	Saponification number	Freezing point (°C)	Pour point (°C)	Flash point (°C; COC)[b]	Fire point (°C; COC)[b]	Color APHA[c]	Color Gardner[d]
Admex 752	NA	0.975	1.4614	130	0.5	NA	NA	-12	285	307	NA	1
Admex 760	NA	1.150	1.4700	117,600	2.5	NA	NA	3	293	329	NA	3
Admex 761	NA	1.110	1.4800	5,330	3.0	NA	NA	2	238	310	NA	3
Admex 770	NA	1.110	1.4660	5,570	2.0	NA	NA	-1	293	316	NA	1
Admex 775	NA	1.095	1.4670	6,130	1.3	NA	NA	-18	288	315	NA	1-
Admex 890	NA	1.097	1.4665	4,890	2.0	NA	NA	2	304	323	NA	1
Paraplex[u] G-25	8,000	1.06	1.470	220,000	1.4	450	15	NA	316	NA	NA	8-[t]
Paraplex G-30	783	1.10	1.501	1,300	0.5	430	-29	NA	257	NA	130	NA
Paraplex G-31	995	1.11	1.503	4,800	0.6	426	-20	NA	274	NA	160	NA
Paraplex G-40	6,000	1.15	1.471	200,000	1.4	585	< -18	NA	288	NA	180[v]	NA
Paraplex G-41	5,000	1.13	1.470	110,000	0.8	550	-22	NA	288	NA	100[v]	NA
Paraplex G-50	2,200	1.08	1.466	2,300	1.4	500	10	NA	280	NA	NA	4
Paraplex G-51	2,175	1.11	1.464	2,100	0.8	553	< -23	NA	> 93	NA	150	NA
Paraplex G-54	3,300	1.08	1.466	5,300	1.1	535	4	NA	300	NA	130	NA
Paraplex G-56	4,200	1.11	1.466	107,000	0.8	562	-10	NA	310	NA	NA	2-
Paraplex G-57	3,450	1.099	1.4661	6,200	0.8	526	1	NA	277	NA	100	NA
Paraplex G-59	4,900	1.127	1.4699	25,400	0.7	571	7	NA	232	NA	NA	4
Uniflex[w] 300	NA	1.009	1.4660	3,330	2.0	NA	NA	NA	293	327	NA	5
Uniflex 312	NA	1.076	1.4650	1,054	2.0	NA	NA	NA	291	313	NA	2
Uniflex 314	NA	1.1924	1.4791	5,970	32.5±2.5	NA	NA	NA	316	338	150	NA
Uniflex 315	NA	1.105±0.005	1.4650	7,293	2.0	NA	NA	NA	279	316	200	NA

continued

TABLE IV-2. (continued)

	Approximate molecular weight	Specific gravity (25/25°C)	Refractive index (25°C)	Viscosity (cps at 25°C)[a]	Acid number (mg KOH/g)	Saponification number	Freezing point (°C)	Pour point (°C)	Flash point (°C; COC)[b]	Fire point (°C; COC)[b]	Color APHA[c]	Color Gardner[d]
Uniflex 320	NA	1.085±0.003	1.4660	2,713	2.0	NA	NA	NA	279	307	NA	7
Uniflex 325	NA	1.100±0.003	1.4650	5,830	2.0	NA	NA	NA	293	332	NA	5
Uniflex 327	NA	1.055±0.003	1.469	2,954	2.0	NA	NA	NA	263	285	200	NA
Uniflex 330	NA	1.088±0.003	1.4660	5,766	2.0	NA	NA	NA	291	318	150	NA
Uniflex 331	NA	0.961±0.005	NA	NA	4.0	NA	NA	NA	291	313	NA	6+
Uniflex 337	NA	NA	NA	NA	10	NA	NA	NA	NA	NA	NA	6+[x]
Uniflex 338	NA	0.998±0.005	NA	3,693	3.5	NA	NA	NA	288	313	NA	7

a cps = centipoise; all values at 25°C except as follows: all Plastolein and Nuoplaz at 38°C and all Morflex at 99°C. See ASTM D 1638-74.
b Most test methods were Cleveland Open Cup. Others did not state the specific method used. See ASTM D 92-66.
c Color APHA = Standards based on dilutions of cobaltous chloride, potassium chloroplatinate, and concentrated hydrochloric acid in water (B. Mills, Monsanto Chemical Company). See also ASTM D 1544-68.
d Color Gardner = A set of 18 solutions; the lightest standard (No. 1) is equal to 0.550 g/liter of potassium chloroplatinate. Each solution is 50% darker than the preceding solution (Gardner and Sword, 1962). See also ASTM D 1554-68.
e Tenneco Chemicals.
f NA = Not available.
g Pfizer Chemicals.
h @(20/20°C).
i Emery Industries.
j Mobay Chemicals.
k Density (g/cm^3).
l Hercules, Incorporated.
m Monsanto Industrial Chemicals Company.
n 50:50 in 95% ethanol.
o Reichold Chemicals.
p @(23/15.5°C).
q Cambridge Industries
r The C. P. Hall Company
s This is the point when the liquid reaches a viscosity of a stiff paste.
t Sherex Chemical Company, Incorporated.
u Rohm and Haas Company.
v 50% solids.
w Union Camp Corporation
x 1% in xylene.

TABLE IV-3. CHEMICAL ABSTRACT NUMBERS FOR POLYESTERS

Compound	Chemical Abstract No.
Adipic acid, polyester with 1,2-propanediol	25101-03-5
Adipic acid, 1,3-butylene glycol, 2-ethylhexanol polymer	63149-79-1
Adipic acid, 1,3-butylene glycol, palmitic acid polymer	30918-39-9
Adipic acid, 1,3-butylene glycol polymer, 2-ethylhexyl ester	69029-19-2
Adipic acid, 1,3-butylene glycol polymer, isodecyl alcohol modified	68441-97-4
Adipic acid, butylene glycol polymer, isodecyl ester	69029-22-7
Adipic acid, palmitate, 1,3-butanediol polymer	69029-21-6
Adipic acid, phthalic anhydride, 1,3-butylene glycol, 1,2-propylene glycol polymer stearate	68238-78-7
Adipic acid, phthalic anhydride, dipropylene glycol resin	9011-80-7
Adipic acid, phthalic anhydride, 1,2-propanediol, 1,4-butanediol polymer, caprylate, caprate	68890-79-9
Adipic acid, phthalic anhydride, 1,2-propylene glycol polymer, diisodecyl ester	68511-08-0
Azelaic acid, polyester with 2,2-dimethyl--1,3-propanediol	29408-58-0
Azelaic acid, adipic acid, propylene glycol, polymer, 2-ethylhexyl ester	68071-01-02
Azelaic acid, propylene glycol polymer	29408-67-1
Sebacic acid, polyester with 1,3-butanediol	28606-47-5
Sebacic acid, polyester with diethylene glycol	25610-21-3
Sebacic acid, polyester with 1,2-propanediol	26222-20-8

Flash Point--

Flash point is the temperature at which a liquid evolves a vapor sufficient to form an ignitable mixture with the air near the surface of the liquid. Most of the tests for the polyesters used the Cleveland Open Cup method. Flash points for most of the linear polyesters were within the range of approximately 230 to 300°C. Published test method was ASTM D 92-66.

Chemical Properties

No studies were found in the literature which were directly related to the chemical properties of linear polyesters in the pure state. As with the epoxy compounds, considerable work has been performed on these materials as components of an overall polymer system. Most testing is done on plastic sheets or film containing polyesters as the plasticizer.

Little information was obtained from the manufacturers and all of it was in general terms with no specific data. Linear polyesters are susceptible to base hydrolysis, usually above pH 8 and at approximately 70-80°C. These compounds, in general, were described by the manufacturers as being relatively stable towards acid hydrolysis and exhibiting good thermal stability. No experimental data or detailed information on acid hydrolysis and thermal stability for specific products was available from the manufacturers.

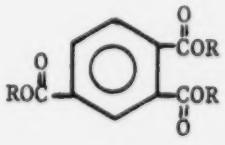
Polyesters are generally unreactive, except as noted above, with other chemicals which would result in degradation of the plasticizer. These materials do not undergo hazardous polymerization. Material Safety Data Sheets supplied by the manufacturers state that polyesters do not decompose at high temperatures to produce any hazardous products except those products normally associated with the burning of organic compounds (CO, CO_2, etc.). Ultraviolet light will degrade the polyesters in vinyl film, but no data are available on the pure polyester or products of the degradation.

TRIMELLITATES

This subsection will present a discussion of the nature of the raw materials and a discussion of the physical and chemical properties of these plasticizers.

Characterization

Trimellitates are esters derived from trimellitic acid (1,2,4-benzenetricarboxylic acid) and alcohols in the range of C_7 to C_{10}. During actual production of these esters, trimellitic anhydride is used instead of the acid. A generalized trimellitate, or trimellitic acid ester, is as shown:



R = C_7 to C_{10}

In terms of characterization, this class of plasticizer is different from either the epoxy compounds or the linear polyesters in that trimellitates represent compounds with definable molecular weights. While many of these materials are esters resulting from 2-ethylhexanol, isooctanol, 1-methyl heptanol, or decanol, mixtures of C_7 to C_9 and C_8 to C_{10} alcohols are commonly used. In this case, the resultant products will be a mixture of esters.

Physical Properties

Each manufacturer of trimellitates was contacted for information relating to the physical properties of their respective products. These data are compiled in Table IV-4. In general, the test methods were not identified. Some manufacturers identified the procedures as ASTM methods. In contrast to the two previous classes of plasticizers, only slightly more than 50% of the manufacturers responded with data on physical properties. For the other two classes, the response was generally greater than 90%.

The few data reported show that, as a class, trimellitates exhibit low vapor pressures even at elevated temperatures. At temperatures of 250-260°C, vapor pressures generally range from 0.2 to 5 mm Hg; at room temperature, the pressures were usually stated to be negligible. Solubility of these esters in water at approximately room temperature ranges from negligible to about 0.1%.

Chemical Abstracts numbers of the commercially significant trimellitates and synopses of selected physical properties are presented in the following subsections.

Chemical Abstracts Service Registry Numbers--

Chemical Abstracts numbers (CAS numbers, CASRN) for those trimellitates which have commercial significance are presented in Table IV-5. Other trimellitates may be listed in compilations such as the TSCA Candidate List of Chemical Substances but were not among the products for which data were supplied by producers or distributors.

Specific Gravity--

The specific gravity for the trimellitates generally fell within the range of 0.97 to 0.99. This is slightly lower than the values observed for the linear polyesters, epoxidized soybean oil, and epoxidized linseed oil. The trimellitates have a bulk weight slightly less than water. Referenced method was ASTM D 1045-80.

Viscosity--

The viscosity of the trimellitates ranged from about 50 to 300 centipoise. This is considerably less than for the linear polyesters and epoxidized linseed oil but about the same as that for epoxidized soybean oil. The octyl epoxytallates have the lowest viscosity values.

Acid Number--

Acid number is a measure of the free acid functionalities present in the product. For trimellitates, the acid numbers range from 0.05 to 0.1. This range is lower than the ranges for any of the other classes of plasticizers and indicates a low level of free acid groups in the finished product.

TABLE IV-4. PHYSICAL PROPERTIES OF TRIMELLITATE PLASTICIZERS

	Approximate molecular weight	Specific gravity (25/25°C)	Refractive index (25°C)	Viscosity (cps at 25°C)[a]	Acid number (mg KOH/g)	Acidity as trimellitic acid (%)	Acidity as acetic acid (%)	Ester content (% min)	Boiling point (3mm Hg; °C)	Freezing point (°C)	Pour point (°C)	Flash point (°C; COC)[b]	Color APHA[c]
PX-337[d]	546	0.987	1.485	220	NA[e]	NA	0.01	99.0	260[f]	NA	-40	254	100
PX-338	546	0.987	1.485	216	NA	NA	0.01	99.0	260[f]	NA	-46	254	100
PX-336	NA	0.972	1.482	103	NA	NA	0.007	99.0	275[f]	-17	NA	278	75
HATCOL TOTH[g]	546	0.987	1.4848	300[h]	NA	NA	0.01	99.0	283	NA	-45	260	75
NUOPLAZ TOTH[i]	546	0.986-0.992	1.4850	NA	0.1	NA	0.1	99.0	283	-46	-32	260	75
KODAFLEX TOTH[j]	547	0.989[k]	1.4832	194	NA	0.02	NA	99.0	600[l]	-38	NA	263	NA
STAFLEX TOTH[m]	547	0.986[n]	1.4855	210	NA	0.010	NA	NA	311	NA	-45	258	75
STAFLEX TIOTH	547	0.986[n]	1.4852	200	NA	0.010	NA	NA	327	NA	-48	258	75
STAFLEX NONDTH	578	0.974[n]	1.4830	90	NA	0.015	NA	NA	335	NA	-7	266	80
Rucoflex 26TH[o]	546	0.992[k]	1.4846	244	0.05	0.02	NA	NA	283	-35	NA	257	150
Rucoflex NTH	560	0.983[k]	1.4829	100	0.05	0.02	NA	NA	289[p]	-45	NA	260	200
Rucoflex C7-C9	NA	0.990[k]	1.4845	NA	0.05	NA	0.017	NA	NA	NA	NA	NA	150
Uniflex TOTH[q]	NA	0.991[k]	1.4830	213	0.1	NA	NA	NA	NA	-35	NA	254	100
Uniflex TCTH	NA	0.977[k]	1.4780	242	0.1	NA	NA	NA	NA	-35	NA	246	100
Santicizer 79TH[r]	548	0.982-0.987	1.481-1.484	113	NA	NA	NA	NA	263[s]	NA	-50	263	100

a cps = centipoise = $\frac{g^m}{sec \times cm}$ x 100; at 20°, the viscosity of water ≅ 1.0 cps.

b Test methods were Cleveland Open Cup. See ASTM D 92-66.

c Color APHA = Standards based on dilutions of cobaltous chloride, potassium chloroplatinate, and concentrated hydrochloric acid in water (B. Hills, Monsanto Chemical Co.). See also ASTM D 1209-79

d USS Chemicals.

e NA = Not available.

f @ 1 mm Hg

g Hatco Chemical Corporation.

h @ 20°C

i Tenneco Chemicals.

j Eastman Chemicals.

k @ 20/20°C.

l @ 760 mm Hg.

m Reichold Chemicals, Incorporated

n @ 23/15.5°C.

o Ruco, Div. Hooker Chemicals.

p @ 1.5 mm Hg

q Union Camp Corporation.

r Monsanto Company.

s @ 10mm Hg.

TABLE IV-5. TRADE AND CHEMICAL NAMES OF TRIMELLITATES

Trade name	Chemical name	CAS number
PX-336	n-octyl, n-decyl trimellitate	34870-88-7
PX-337	triisooctyl trimellitate	27251-75-8
PX-338	trioctyl trimellitate	89-04-3
HATCOL TOTM	tri(2-ethylhexyl)trimellitate	3319-31-1
NUOPLAZ TOTM	tri(2-ethylhexyl)trimellitate	3319-31-1
KODAFLEX TOTM	tri(2-ethylhexyl)trimellitate	3319-31-1
STAFLEX TOTM	1,2,4-benzenetricarboxylic acid; 2-ethylhexyl ester	68186-31-2
STAFLEX TIOTM	1,2,4-benzenetricarboxylic acid; isoctyl ester	68186-32-3
STAFLEX NONDTM	1,2,4-benzenetricarboxylic acid; octyl, decyl ester	34870-88-7
RUCOFLEX 26-TM	tri(2-ethylhexyl)trimellitate	3319-31-1
RUCOFLEX NTM	tri(mixed-n-alkyl)trimellitate	not listed
RUCOFLEX C7-C9	tri(C-7, C-9 alkyl)trimellitate	68515-60-6
UNIFLEX TOTM	tri(2-ethylhexyl)trimellitate	3319-31-1
UNIFLEX TCTM	tri(1-methylheptyl)trimellitate	not listed
SANTICIZER 79-TM	tri(C-7, C-9 alkyl)trimellitate	68515-60-6

Flash Point--

For the trimellitic acid esters, the flash points are in the range of 245 to 280°C. This range is lower than that for epoxidized soybean oil and linseed oil and approximately the same as for the linear polyesters. Octyl epoxytallates had the lowest flash point range. Measurements for the trimellitics were by the Cleveland Open Cup method. Procedure stated to be ASTM D 92-66.

Chemical Properties

No studies were found in the literature which were directly related to the chemical properties of trimellitates in the pure state. In contrast to the other two classes of plasticizers, little information was found on chemical properties of these materials as components of an overall polymer system.

In general, the data supplied by the manufacturers and distributors were approximately the same as for the epoxy compounds and the linear polyesters. Trimellitates are incompatible with oxidizing agents and nitric acid. They are hydrolyzed by alkali, but usually temperatures of about 100°C are required. The trimellitates are more resistant to acid hydrolysis by non-oxidizing acids than to hydrolysis by alkali. Manufacturers would provide no experimental details on the alkali or acid hydrolysis data. No hydrolysis of these esters was found after 96 hr in boiling water.

Trimellitates exhibit little additional incompatibility with other chemicals which would result in degradation of the plasticizer. These materials do not undergo hazardous polymerization. In general, the compounds show good thermal stability with only 0.04% decomposition to the corresponding acid after heating the pure compound for 2 hr at 200°C. However, at higher temperatures, more rapid dissociation to the corresponding acid may occur, which can present potential health problems for local personnel. This aspect will be discussed more thoroughly in the section concerned with health effects (Section VI).

SECTION V

PRODUCTION AND USE

This section contains information on the production locations, quantities manufactured, production methods, plasticizer uses, estimated worker exposure, occupational standards, and environmental transport and degradation. Information is provided for each of the three classes of plasticizers included in this study.

EPOXY COMPOUNDS

Producers and Quantities

A listing of the manufacturers of epoxidized plasticizers, their production locations, and production method is shown in Table V-1. The largest volume producers of this class of plasticizer are Union Carbide Corporation, Witco Chemical Corporation, and Rohm and Haas Company. These three producers account for approximately 75% of the total production capacity for the industry, which is an estimated 245 million pounds per year.

The estimated annual U.S. production quantities for epoxidized plasticizer are presented in Table V-2 for 1975-1979. During that time period, the overall production trend was towards increased production of this class of plasticizer. Industry sources estimated that the data in Table V-2 are accurate to ± 10%. However, the production of 130 million pounds in 1979 represents only approximately 50% of the total operating capacity of the industry (Sigan, 1980). Preliminary data in Modern Plastics indicated that for 1980 the estimated consumption of epoxy plasticizers will be about 121 million pounds, which is a decrease of approximately 9 million pounds from 1979. Manufacturers indicated that annual production is approximately equal to consumption and that little stockpiling occurs.

Production Process

The principal epoxidized plasticizer products currently produced in the United States are derived from vegetable oil substrates (e.g., soybean oil) or from alkyl fatty acid ester substrates, (such as octyl esters of tall oil fatty acids (Lutz, 1980).

Epoxidation is defined as a chemical reaction in which double bonds in unsaturated (e.g., olefinic) compounds are converted to cyclic three-membered ethers by an active oxygen agent. This is shown schematically the following equation (Thompson, 1977).

TABLE V-1. MANUFACTURERS OF EPOXY PLASTICIZERS

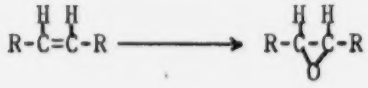
Company	Production site	Production method
Rohm and Haas Co.	Philadelphia, PA	P.F.[a]
Union Carbide Corp.	Taft, LA	P.A.[b]
Witco Chemical Corp.	Taft, LA	P.A.
Viking Chemical Co.	Blooming Prairie, MN	P.A.
FMC Corporation	Bayport, TX	P.A.
Ferro Chemical Co.	Bedford, OH	P.F.
Sherex Chemical Co.	Mapleton, IL	P.A.
Swift Specialty Chemical Co.	Griffith, IN	N.A.

[a] P.F. = Performic acid
[b] P.A. = Peracetic acid
[c] N.A. = not available

TABLE V-2. ANNUAL PRODUCTION OF EPOXY PLASTICIZERS
(million pounds)

Plasticizer	1975		1976		1977		1978		1979	
	ITC[a]	MP[b]	ITC	MP	ITC	MP	ITC	MP	ITC	MP
Total Epoxy	97.6[c]	117	117.4	117	120.5	119	120.2[d]	126	N.A.[e]	130
Soybean Oil	77.6	-	91.4	-	92.5	-	89.9	-	-	-
Linseed Oil	N.A.	-	6.4	-	5.2	-	6.4[f]	-	-	-
All others[g]	20.0	-	19.6	-	22.8	-	23.9	-	-	-

[a] ITC = International Trade Commission data.
[b] MP = Modern Plastics data.
[c] Does not include epoxidized linseed oil.
[d] Sum includes linseed oil sales data.
[e] N.A. = not available.
[f] Data are for sales of epoxidized linseed oil.
[g] Primarily epoxytallate esters.



The principal oxygen sources for this conversion are peracetic acid or performic acid. Both peracids result from treatment of the normal acids with hydrogen peroxide (Thompson, 1977).

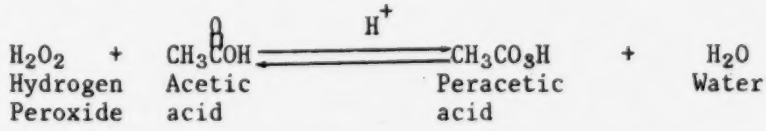
In the United States, epoxidized plasticizer materials are produced primarily by reacting the unsaturated substrate with either peracetic acid (peroxyacetic acid) or with performic acid (peroxyformic acid) (Lutz, 1980). Peracetic acid can be prepared by the oxidation of acetaldehyde with hydrogen peroxide. Performic acid can be prepared by a similar oxidation of formaldehyde. Although the use of performic acid is discussed in the literature, peracetic acid is the principal reagent in the use at the present time.

Epoxidation processes used in the United States can be divided into two basic types: either the peracid is preformed or it is formed in situ, (i.e., in a primary reaction vessel) (Lutz, 1980). At present epoxy plasticizer production in the United States is roughly evenly divided between these two processes. Batch production methods are used extensively for both processes. Each process has its own advantages and disadvantages. The product composition and performance can be affected by proprietary processes involving peracid formed in situ or preformed peracid using co-solvents, especially selected olefinic substrates and catalysts, methods of addition of components, and post-treatment of the epoxide (Lutz, 1980).

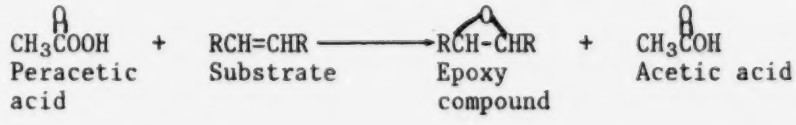
Figure V-1 shows a representative schematic of the general process flow arrangement used for each of the two basic production processes. A discussion of these process methods follows.

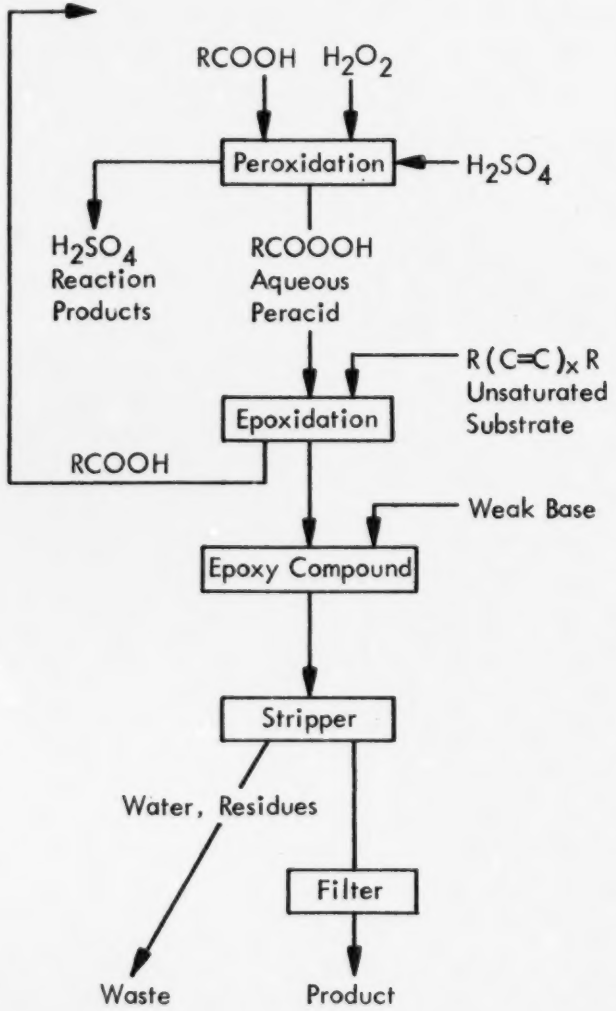
Epoxidation with Preformed Peracid--

Peracid is formed as the first step (peroxidation) in this process, as shown in Figure V-1a. For example, peracetic acid can be prepared from acetic acid and hydrogen peroxide according the following reaction:

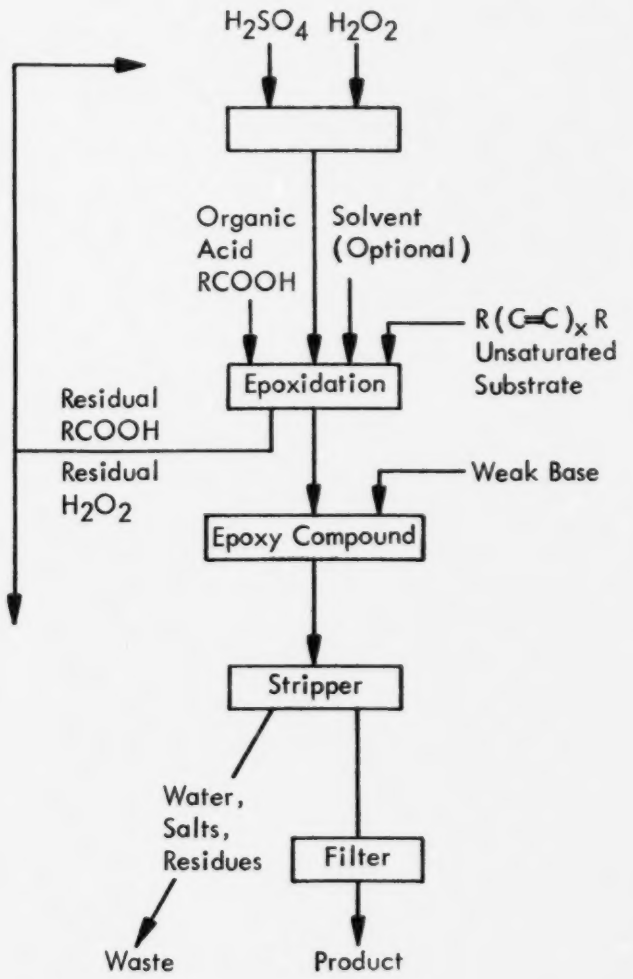


In this process, using preformed peracetic acid, a catalyst is not necessary for the epoxidation step and the reaction can be conducted at 20° to 80°C according to the reaction:





a. Preformed Acid Process



b. In Situ Process

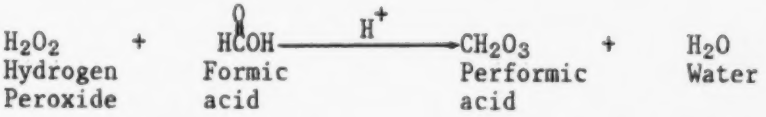
Source: Midwest Research Institute

Figure V-1. Schematic of the two basic epoxidation processes.

By-product acetic acid is recycled to the peroxidation step. The epoxy compound is combined with a weak base and treated in a stripper to separate water and residues as waste materials. The crude product is then filtered to yield the final purified product. A major disadvantage of this process is the fact that the preformed acid presents an explosion hazard and cannot be safely stored (Lutz, 1980).

Epoxidation with Peracid Formed in situ--

Many production techniques for in situ epoxidation have been developed. In general, a peroxide solution (35 to 70% of hydrogen peroxide in water) containing a small amount of a mineral acid catalyst (e.g., sulfuric acid or phosphoric acid) is added to a mixture of an epoxidizable substrate and acetic acid or formic acid. As the reactants are mixed, hydrogen peroxide and the organic acid react in the presence of the acid catalyst to form the peracid. An example, with formic acid and hydrogen peroxide as reactants, is shown in the following reaction:



The peroxide solution is added incrementally with agitation to prevent an uncontrolled exothermic reaction. The reaction temperature is maintained at 50° to 65°C for 10 to 40 minutes per addition of peroxide. Using this operating procedure, only small amounts of peracid are formed in the presence of the unsaturated substrate. Since the peracid reacts with the unsaturated portion of the molecule, the peracid is quickly depleted and a buildup of detonatable quantities of peroxide compounds is avoided.

After the iodine number of the substrate is reduced to a predetermined level, the reaction is stopped and the epoxidized substrate is separated from an aqueous layer. This aqueous layer, which contains a mixture of organic peracid and some hydrogen peroxide, can be recycled to the next batch as part of the charge. In the epoxy material, the acid catalyst is neutralized with a mild base, and residual peroxide is decomposed. The crude epoxy compound is then washed and transferred to a stripper for removal of water and nonproduct residues. Following the stripping step, the epoxy compound is purified in a filtration step to obtain the finished product.

As a process option, solvents compatible with the substrate can be used to facilitate epoxidation. For example, heptane or octane serve well with soybean oil substrate and aromatic solvents (e.g., toluene) can be used with linseed oil (Lutz, 1980).

Process Modifications--

There are a number of modified production processes based on the two general processes. A brief discussion of two of the most common is presented in the following paragraphs.

Processes using sulfuric acid as catalyst--In situ production methods for epoxidation of soybean oil based on use of acetic acid with sulfuric acid as catalyst have been developed by the Archer-Daniels-Midland (ADM) Company and the FMC Corporation (Lutz, 1980).

In the ADM process, the catalyst is added last and is admixed with glacial acetic acid. Epoxy ring opening by the sulfuric acid is minimized since the system is heterogeneous and involves the interaction of an oil phase and an aqueous phase containing acetic acid and hydrogen peroxide.

In the FMC modification of the basic in situ process, an inert solvent (e.g., hexane) is used to reduce the effect of sulfuric acid in catalyzing epoxy ring opening.

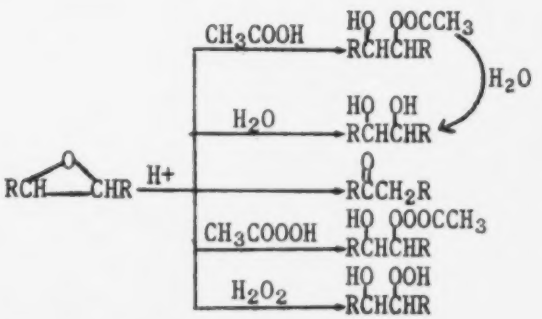
Repeated-resin process--In this process, a relatively large quantity of poly(styrenesulfonic acid) resin is used as catalyst; however its reuse is required in succeeding epoxidation batches to achieve good economics. Advantages claimed for this process include high epoxy yields, little by-product formation, almost complete elimination of unsaturation, low reaction temperatures (60°C), and short reaction periods (Lutz, 1980).

The process involves mixing the fatty oil or ester, glacial acetic acid acid, and dry resin. Hydrogen peroxide is added slowly so that a reaction temperature of 60°C is not exceeded. The reaction medium is maintained at the maximum temperature for about 4 hr and then separated from the resin catalyst by decantation or filtration. The resin catalyst remains in the reactor for succeeding runs. The catalyst can be reused for approximately 6 to 8 runs. With each succeeding run, degradation of the catalyst produces fine particles which may introduce problems in the filtration procedures.

If products with maximum epoxy oxygen values are not required, the general practice is to use much less resin. A smaller amount of resin can be economically discarded following each run. This procedure is termed the minimal-resin technique.

By-Products and Contaminants--

The only major contaminants in the product plasticizer are by-products formed during the process reaction. Since the epoxidation process is reversible, there is a potential for the occurrence of undesirable side reactions. Although the epoxidation reaction is generally conducted at the lowest temperature and shortest time consistent with the desired product, the following side reactions can occur (Lutz, 1980).



The specific composition of the by-product mixture will vary considerably depending upon the specific reaction process, reaction temperature, pressure, and other variables. According to a major epoxy manufacturer, the two by-products at the top, the hydroxy ester and the glycol, would probably constitute the major components of most by-product mixtures. If the by-products are not volatile (almost none are volatile), they are processed with the epoxy compound and will remain in the final product. For most reaction processes, the approximate quantity of by-product found is less than 5% of the total product material.

Production Losses--

Industry sources estimate that the overall loss of plasticizer due to processing and transfer is approximately 2% of the total production quantity. The losses occur during four processes: stripping, filtering, neutralization, and washing. The largest contribution to product loss probably occurs in the filtering process and the next largest is in stripper losses. No information is available concerning the actual quantities lost by each process. Losses resulting from neutralization and washing are estimated to be very small and probably less than losses from the stripper. The filter material containing the epoxy plasticizer is likely disposed in a landfill.

Uses

Epoxy plasticizers are usually employed as secondary plasticizers, which means they are always used in conjunction with other plasticizers to provide specific properties to the finished plastic or to perform certain functions within the plastic matrix.

Information from manufacturers varied with respect to the percentage utilization of epoxy plasticizers. No published data were available regarding the quantities of epoxy compunds used in specific products. The following estimate represents a combination of data from several manufacturers, not the views of any single company.

Use Category	%	Quantity in 1979 (million pounds)
Polyvinyl chloride	85-90	111-117
Other polymers	8-13	10-17
Miscellaneous	2	3

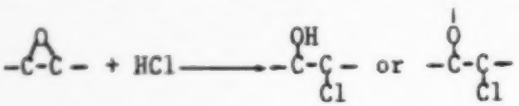
Other polymeric systems included nitrocellulose, chlorinated rubber, chlorinated polyethylene, and acrylics. Miscellaneous uses include adhesives, sealants, pesticide formulations, and a myriad of uses employing small volumes. Usage of epoxy plasticizers in adhesives and sealants is for purposes of stabilization; very small quantities are employeed in this area. No published information was found relating to uses of epoxy compounds in specific products of polyvinyl chloride (PVC). Producers stated that epoxy compounds are used to impart good flexibility properties, particularly at lower temperatures, and good hydrogen chloride stability. One specific area of use for epoxy compounds is with flat vinyl film or sheet, including film for food wrapping.

The use of epoxy compounds as secondary plasticizers can be exemplified by considering the change in formulation which would occur. A standard PVC formulation for a flexible film and a formulation employing a secondary plasticizer are as shown:

Standard Formulation		Formulation with Epoxy	
PVC resin	: 100 parts	PVC resin	: 100 parts
Plasticizer (e.g. DOP[a])	: 50 parts	Plasticizer (eg. DOP)	: 45 parts
Stabilizer	: 3 parts	Epoxy Compound	: 5 parts
		Stabilizer	: 3 parts

DOP=dioctyl phthalate

Epoxy plasticizers are very good acid stabilizers and react readily with hydrogen chloride which is generated in the PVC as the plastic degrades. As stated in the discussion of chemical properties (Section IV), epoxide rings are quite susceptible to ring opening due to acid attack. The action of hydrochloric acid, or hydrogen chloride, on the epoxide ring can result in formation of the corresponding hydroxy chloro compound or formation of a cross-linked chloro ether, as shown in the following equation:



If the ether cross-linkage becomes extensive within the plastic, loss in flexibility and production of a brittle product could result.

Quantities Released During Processing--

Essentially all processes used with the high volume production of formulated PVC resins are highly automated. Wilkinson, et al. (1979) performed an extensive study of the production and use of selected aryl and alkyl aryl phosphate esters. In this study, no evidence was found of any consistent loss of plasticizer during resin formulation. Losses due to equipment malfunction or breakage occur but are very difficult to quantify. Since both phosphate esters and epoxy compounds are used primarily with PVC resins and both are liquids, the processing methodologies should be very similar.

Ultimate Disposal--

Although the useful life of plastics varies considerably from one product to another, most plastic products will be discarded within a relatively short period of time (a few years). These plastics will become solid waste and subjected to either incineration or landfill. The very low volatility of the epoxy plasticizers and their very low migration from plastics would preclude any appreciable loss of the plasticizer from the product during its use. However, plasticizers can migrate from one plastic to another if their solubility in the second plastic is greater.

It has been estimated that of the phthalate plasticizer containing plastics that are disposed of as solid waste, 10 to 20% are destroyed by high temperature incineration and 2% are subjected to low temperature incineration or open burning (Peakall, 1975). The remainder of the plastic would be disposed in a landfill. Since epoxy compounds are employed as secondary plasticizers, often with phthalates, these disposal figures would appear to be valid for this class of plasticizer. Within the landfill, the epoxy plasticizers are subject to rapid attack by fungi and bacteria (see Section VI, Environmental Effects). The exact lifetime of the epoxy compounds in the landfill is unknown, but probably is less than 2-3 years based on the microorganism degradation studies reported in Section VI.

Worker Exposure and Occupational Standards

Occupational Standards--

No information was found concerning any occupational standards for epoxy plasticizers. Sources searched for these data were the National Institute for Occupational Safety and Health (1978a, 1978b), American Conference of Governmental Industrial Hygienists (1979), and Sittig (1979).

Worker Exposure--

The National Institute for Occupational Safety and Health (1980) has estimated the total number of workers exposed to certain chemicals in plants of selected industries. This National Occupational Hazard Survey (NOHS) estimated that a total of 1,257,364 workers covering 202 occupations were exposed to one or more plasticizers. NOHS estimated that a total of 264,112 workers covering 177 occupations were exposed to epoxy plasticizers. The individual data are as follows (number of workers rounded as appropriate by MRI):

Epoxy Compound	Number of Occupations	Estimated Workers Exposed
Epoxidized oils	100	232,700
Epoxyesters	57	28,000
Epoxidized butyl oleate	18	3,400
Epoxytallates	2	70
Total	177	264,170

It is entirely possible that overlap has occurred in the number of occupations and therefore in the total number of exposed workers. However, it would be extremely difficult to resolve this overlap because insufficient information is presented in the survey.

Environmental Transport and Degradation

Very few quantitative data were found for properties which would be directly related to environmental transport and bioaccumulation. Epoxy plasticizers have very low vapor pressures at ambient conditions so that volatility would not be a major factor in their transport through the environment. In addition, these plasticizers exhibit a very low solubility in water. No

information was available on mobility in soils or sediments. No data were available for octanol-water partition coefficients so that no inferences can be made with respect to bioaccumulation or biomagnification.

Environmental degradation can occur by photolysis, hydrolysis, and biological methods. As discussed in Section IV, no photolytic data are available for pure epoxy compounds, but plastics containing these plasticizers were subjected to photolytic degradation. It was determined that the epoxy plasticizer was being degraded but no products were identified. In the same section, the conditions for hydrolysis were also discussed. The effects of fungi and bacteria on this class of plasticizer are discussed in Section VI, Environmental Effects.

LINEAR POLYESTERS

Producers and Quantities

A listing of the manufacturers of linear polyester plasticizers and their production sites, as supplied by the companies, are shown in Table V-3.

TABLE V-3. MANUFACTURERS OF POLYESTER PLASTICIZERS

Company	Production site
Emery Industries, Inc.	Cincinnati, OH
Rohm and Haas Company	Philadelphia, PA[a]
	Knoxville, TN
Monsanto Company	Everett, MA
Reichold Chemicals, Inc.	Carteret, NJ
C.P. Hall Company	Chicago, IL
Pfizer, Inc.	Greensboro, NC
Union Camp Corporation	Dover, OH
Cambridge Industries	N.A.
Sherex Chemical Co.	Mapleton, IL

N.A. = not available.
[a] Believed to have discontinued production at this site in 1980.

The largest volume producers are Emery Industries and Rohm and Haas. Industry sources estimate that the combined market shares of these two companies probably account for approximately 60% of the total market with the remaining seven companies sharing 40% of the market. Production capacity data are very difficult to ascertain because the plants are multipurpose facilities capable of producing many types of ester plasticizers.

The estimated annual U.S. production levels for polyester plasticizers are presented in Table V-4 for 1975-1979. One industry source stated that the International Trade Commission production figures for adipic acid type should actually be 37.5 and 42.0 million pounds, respectively, in 1977 and 1978. This source also estimated that only approximately 40-45 million pounds of the polyester during 1977 to 1979 is being use for plasticizer purposes and the remainder is starting material in urethane foams.

TABLE V-4. ANNUAL PRODUCTION OF POLYESTER PLASTICIZERS
(million pounds)

Plasticizer	1975		1976		1977		1978		1979	
	ITC[a]	MP[b]	ITC	MP	ITC	MP	ITC	MP	ITC	MP
Total Production	38.4	46	52.9	51	48.0	53	54.2	53	N.A.[c]	55
Adipic Acid Type	-	-	33.3	-	10.5	-	12.2	-	-	-
All Other	-	-	19.6	-	37.5	-	42.0	-	-	-

[a] ITC = International Trade Commission data
[b] MP = Modern Plastics data
[c] N.A. = not available

Preliminary data in Modern Plastics indicate that for 1980, the estimated consumption of polyester plasticizers will be about 48.5 million pounds, which represents a decrease of approximately 6 million pounds from 1979. Manufacturers indicate that annual production is approximately equal to consumption and that little stockpiling occurs.

Production Process

Linear polyesters, which are also known as polymeric plasticizers, are produced by the polymerization/esterification of an aliphatic dicarboxylic acid, or acid anhydride, with either pure or mixed aliphatic alcohols (glycols). The dicarboxylic acids commonly used include adipic, sebacic, and azelaic. Phthalic anhydride is believed to be used in certain instances. Glycols are usually propylene glycols or butylene glycols. Ethylene glycol is seldom used because it gives a solid product. Terminating alcohols and acids include stearic acid, oleic acid, 2-ethylhexanol, isodecanol, and many others.

The method of production stems from the basic esterification reaction, but is more complex. In general, the reaction is between a dibasic acid and a dihydric alcohol, usually at an elevated temperature (e.g., $\geq$ 200°C). Variations in the reactants used, rather than the mode of preparation, determine the structure and properties of the polyester. An excess of dihydric alcohol gives a polyester with terminal hydroxyl groups, whereas an excess of dibasic acid gives terminal carboxyl groups. Thus, the chain length of the product can be varied by changing the proportions of the reactants. The use of a monohydric alcohol or a monobasic acid as a third reactant limits the chain growth and provides esters which are termed "alcohol end-stopped"

and "acid end-stopped", respectively. If equimolar amounts of acid and alcohol are used, the reaction is non-end-stopped and usually leads to the production of higher molecular weight polymers. This condition, along with an increase in viscosity, can be achieved by prolonged heating. The average molecular weight of common ester products is about 2,000. Products with average molecular weights of 800 to well over 6,000 are produced for specialty applications.

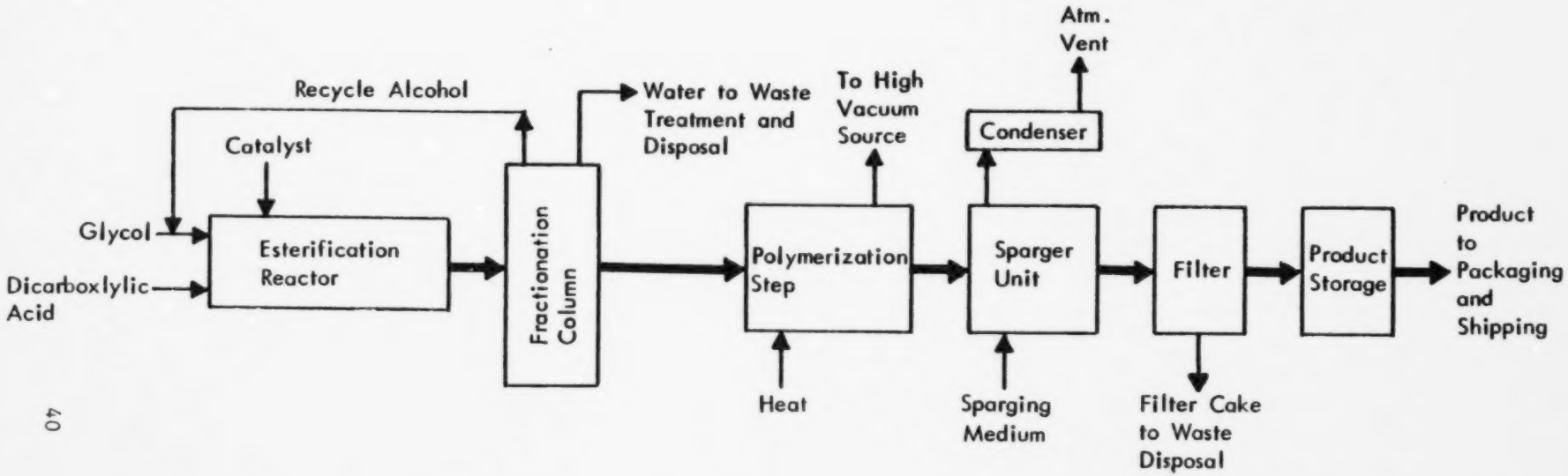
The polymeric esters have greater permanence as plasticizers than do monomeric plasticizers (e.g. dioctyl adipate) because they have very low volatility, low extractability by solvents, and low tendency to migrate into other organic materials. Thus, polymeric plasticizers have found wide commercial acceptance for those applications in which durability and stability are primary considerations.

Most polymeric plasticizers are synthesized by simple esterification reactions, which can be conducted in the liquid phase using heated reaction vessels with stirring and water take-off provisions (Thompson, 1977). The production operations are conducted using batch processess.

A generalized process flow diagram for production of linear polyesters is shown in Figure V-2. The feed materials, consisting of a dicarboxylic acid and an aliphatic dihydric alcohol (glycol) are fed into a esterification reactor. The reaction is usually conducted at a temperature of about 200°C. In some processes a catalyst (e.g., sodium acetate) may be used. An excess (30 to 40%) of glycol is used in carrying out this reaction. A fractionating column is operated in conjunction with the reactor to separate by-product water and unreacted glycol from the reaction mixture. Separated water is sent to waste treatment and disposal; the recovered glycol is recycled to the esterification step. The crude esterification product, which has a low acid number, is sent to a polymerization step.

The polymerization step is carried out by a suitable combination of applied heat and high vacuum to accomplish an ester interchange. The process temperature is normally held at about 200°C. Some of the initial reaction product consists of an undesirable material with the generalized designation of T-G-T, in which G is the glycol and T is a monobasic terminator acid. The purpose of this step is to convert the T-G-T material and other low molecular weight esters to a desired crude product with the formula of $T(G\text{-}A\text{-}G)_x T$, in which A is a dibasic acid by ester interchange. The goal of this step is to drive this ester interchange to obtain a minimum of 90% completion of reaction.

The liquid reaction material discharged from the polymerization step is treated in a sparger unit to separate residual trace amounts of alcohol and odoriferous components. The sparging medium may consist of a high boiling liquid, a noncondensable gas, or steam. The overhead material from the sparger passes through a condenser to a vent; recovered glycol can be recycled to the esterification step. When steam is used as the sparging material, steam condensate is withdrawn from the sparger and sent to wastewater treatment and disposal.



Source: Midwest Research Institute

Figure V-2. Generalized process flow diagram for linear polyesters.

From the sparger unit the liquid reaction product is sent to a filter for removal of suspended matter and turbidity. A filter aid (e.g., diatomaceous earth) is commonly used in this filtering operation. Activated carbon can also be used in this step to absorb undesirable components (e.g., the color of the product can be controlled). The used filter cake is either sent to a landfill or used as an ingredient in the compounding of PVC resin. The product is stored in dedicated storage tanks equipped with heaters and special transfer pumps. The product is withdrawn from storage and sent to packaging and shipping operations.

Multipurpose production equipment is commonly used in U.S. facilities so that plasticizer products other than linear polyesters can be manufactured in the same equipment.

By-Products and Contaminants--

The data compiled from manufacturers for product specification indicate a general product purity for polyesters of 99.5% or higher. The principal contaminants in the finished product generally consist of partially reacted starting material and, in some cases, traces of catalyst residue. Even though the polymerization catalyst is generally removed by chemical reaction, some traces may remain with the polyester.

The sole by-product of this reaction sequence consists of water of esterification formed in the first process step. This water is removed by distillation, with only trace amounts of polyester carried over with the water.

Production Losses--

Industry sources estimate that the overall loss of plasticizer due to processing and transfer is approximately 2% of the total production quantity. The losses occur during three processes: fractionation, filtration, and sparging. The largest contribution to product loss probably occurs in the filter process, followed by the sparging losses. No information is available concerning the actual quantities lost by each process. Losses resulting from the fractionation are estimated to be very small and probably less than from the sparging process. The filter material containing the polyester plasticizer is either disposed in a landfill or used in PVC compounding.

Uses

Linear polyesters are employed principally as primary plasticizers which require very low volatility, low oil or water extraction, and low migration characteristics from the plastic. Information from manufacturers varied with respect to the percentage utilization of the polyesters. No published data were available regarding the quantities of polyesters used in specific products. The following estimate of polyester use as a plasticizer represents a combination of information from several sources.

Use Category	%	Quantity in 1979 (million pounds)
Polyvinyl chloride	~85	38
Rubber	8-10	4-5
Adhesives	4-5	~2
Coatings	1-2	~1

The quantities used in 1979 are based on a volume of 45 million pounds, as indicated by a manufacturer as the level employed for plasticizers.

Uses of polyvinyl chloride which employ polyesters as plasticizers include gaskets for appliances, refrigerators, and automotive vehicles, high temperature wire coatings, high quality vinyl upholstry, electrical tape, coaxial cable coatings, applications requiring oil and gasoline resistance, coated fabrics, apparel and footware, and many others. Food uses of polyester-plasticized PVC include food wrapping film, beverage hoses, milk tubing, milking machine components, bottle cap liners, and food conveyor belting.

Applications of polyesters in the rubber industry as a plasticizer include primarily those areas in which the vulcanizate requires good resistance to swelling and plasticizer migration. Typical rubbers using polyesters include styrene-butadiene and nitrile.

Adhesive applications are in areas such as pressure sensitive adhesive backings and hot melt adhesives. Coating applications include usage of the polyesters as pigment grinding vehicles and dispersion agents.

Quantities Released During Processing--

Essentially all processes used with the high volume production of formulated PVC resins and synthetic rubber are highly automated and employ automatic equipment and pumping systems for liquid plasticizers. No information was available from the literature or industry concerning quantities released during the formulation of resins or rubbers. Since the use of automated equipment usually precludes consistent loss, it is estimated that processing in the plastics and rubber industry does not lead to significant release of polyester plasticizer. Losses due to equipment malfunction or breakage occur but are very difficult to quantify.

No information was found concerning losses during processing in the adhesives or coatings industries. Losses in adhesive applications and in coatings applications would be anticipated to be small due to the physical nature of the polyesters and the volume of material employed in these two industries. In general, polyesters are viscous liquids with a very low vapor pressure and are not easily volatilized. These properties are not conducive to significant losses in situations where mixing would be the principal process. In addition, the estimated overall use of polyesters in these two areas is quite small compared to the uses in PVC resins and synthetic rubbers.

Ultimate Disposal--

Although the useful life of plastic and rubber products varies considerably from one product to another, most products will be discarded within a relatively short period of time (a few years). These products will be solid waste and subjected to either incineration or landfill. The very low volatility of the polyester plasticizers and their very low migration from plastics would preclude any appreciable loss of the plasticizer from the product during its use.

It has been estimated that of the phthalate plasticizer containing plastics that are disposed of as solid waste, 10 to 20% are destroyed by high temperature incineration and 2% are subjected to low temperature incineration or open burning (Peakall, 1975). The remainder of the plastic would be disposed in a landfill. Since polyester plasticizers are employed in many of the same applications as phthalates, these disposal figures would appear to be valid for this class of plasticizer. Within the landfill, the polyester plasticizers are subject to rapid attack by fungi and bacteria. The exact lifetime of the polyesters in the landfill is unknown but probably is less than 2-3 years based on the microorganism degradation studies reported in Section VI.

Worker Exposure and Occupational Standards

Occupational Standards--

No information was found concerning any occupational standards for polyester plasticizers. Sources searched for these data were the National Institute for Occupational Safety and Health (1978a, 1978b), American Conference of Governmental Industrial Hygienists (1979), and Sittig (1979).

Worker Exposure--

The National Institute for Occupational Safety and Health (1980) has estimated the total number of workers exposed to certain chemicals in plants of selected industries. This National Occupational Hazard Survey (NOHS) estimated that a total of 1,257,364 workers covering 202 occupations were exposed to one or more plasticizers. NOHS estimated that a total of 161,500 workers covering 74 occupations were exposed to polyester plasticizers.

Environmental Transport and Degradation

Very few quantitative data were found for properties which would be directly related to environmental transport and bioaccumulation. Polyester plasticizers have very low vapor pressures at ambient conditions, so that volatilility would not be a major factor in their transport through the environment. In addition, these plasticizers exhibit a very low solubility in water. No information was available on mobility in soils or sediments.

No data were available for octanol-water partition coefficients; therefore, no inferences can be made with respect to bioaccumulation or biomagnification.

Environmental degradation can occur by photolysis, hydrolysis, and biological methods. As discussed in Section IV, no photolytic data are available

for pure polyester compounds but plastic containing these plasticizers have been subjected to photolytic degradation. It was determined that the plasticizer was being degraded but no products were identified. In the same section, the conditions for hydrolysis were also discussed. The effect of fungi and bacteria on this class of plasticizer is discussed in Section VI, Environmental Effects.

TRIMELLITATES

Producers and Quantities

A listing of the U.S. manufacturers of trimellitates (trimellitic acid esters) and their production sites, as supplied by the companies, are shown in Table V-5. The large volume producers are reported to be Hooker Chemical, Reichhold Chemicals, USS Chemicals, Monsanto, and Technor-Apex.

TABLE V-5. MANUFACTURERS OF TRIMELLITATE PLASTICIZERS

Company	Production site
Hooker Chemical Corporation	Hicksville, NY
Reichhold Chemicals, Inc.	Carteret, NJ
USS Chemicals, Div. of U.S. Steel	Neville Island, PA
Monsanto Company	Everett, MA
Technor-Apex[a]	Hebronville, MA
	Brownsville, TN
C.P. Hall Company	Bedford Park, IL
Inolex Corporation	Philadelphia, PA
Tenneco Chemicals, Inc.	Fords, NJ
Eastman Kodak Company	Kingsport, TN
Pfizer, Inc.	Greensboro, NC
Exxon	Baton Rouge, LA
BASF Wyandotte Corp.	Kearny, NJ

a Technor-Apex produces trimellitates under contract to other companies and does not offer these plasticizers for direct sale to consumers.

These five companies are estimated to control approximately 90% of the current market. The remaining seven companies control a very small share of the market. Since trimellitates are generally manufactured using multipurpose process equipment capable of producing many other esters, it is very difficult to estimate plant capacities.

The estimated annual U.S. production levels for trimellitate plasticizers are presented in Table V-6 for 1975-1979. Preliminary data in Modern Plastics indicated that for 1980, the estimated consumption of trimellitate plasticizers will be approximately 28.7 million pounds. This represents a decrease of slightly more than 2 million pounds from 1979. Manufacturers indicate that annual production is approximately equal to consumption and that little stockpiling occurs for this class of plasticizer.

Production Process

Trimellitate plasticizers are monomeric compounds and consist of esters of trimellitic acid. The production process is normally conducted on a batch basis. The basic raw material used in the manufacture of these plasticizers is trimellitic anhydride, derived from trimellitic acid.

TABLE V-6. ANNUAL PRODUCTION OF TRIMELLITATE PLASTICIZERS
(quantities in million pounds)

Plasticizer	1975		1976		1977		1978		1979	
	ITC[a]	MP[b]	ITC	MP	ITC	MP	ITC	MP	ITC	MP
Total Trimellitates	16.2	20	23.1	24	27.3	26	32.8	31	N.A.[c]	31
Trioctyl Ester	6.1	-	9.3	-	12.5	-	15.8	-		-
Tri-n-octyl, n-decyl Ester	N.A.	-	N.A.	-	1.2	-	1.1	-		-
All other	10.1	-	13.8	-	13.6	-	15.9	-		-

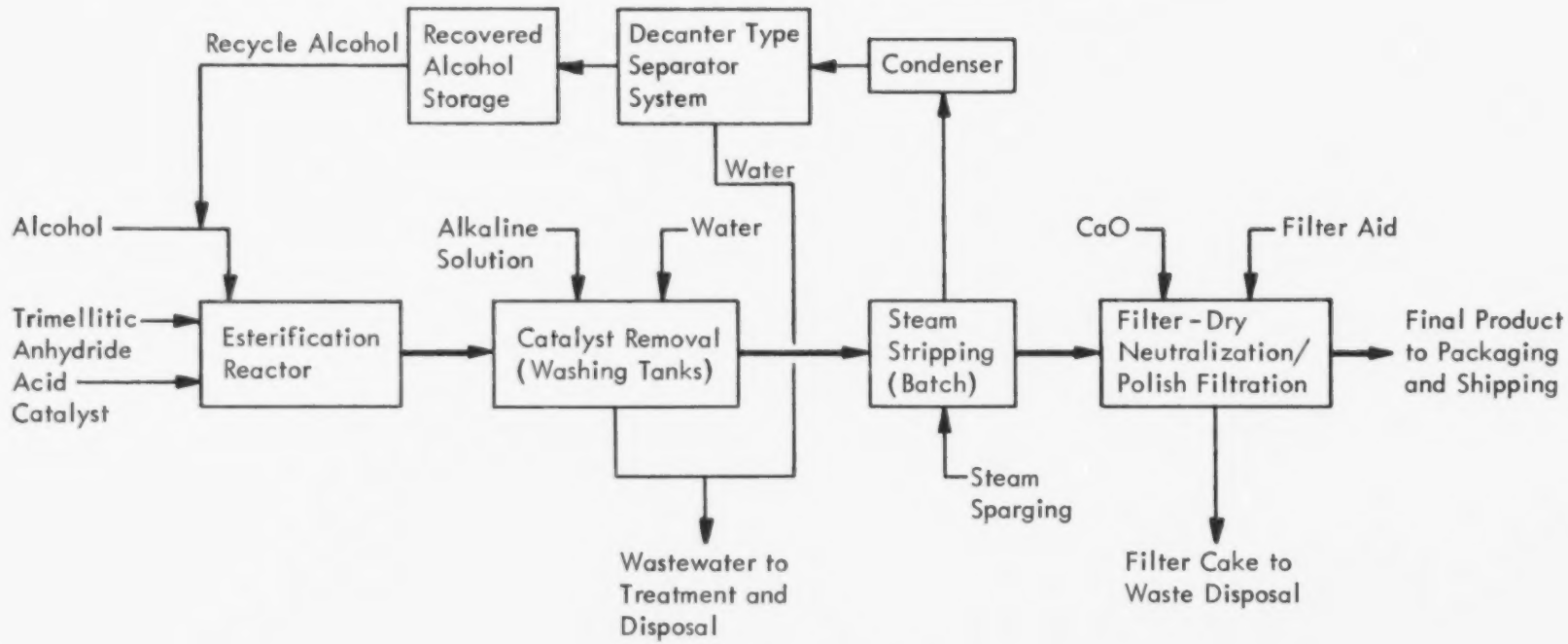
a International Trade Commission data.
b Modern Plastics data.
c N.A. = not available.

The typical production process in the United States is essentially the same as that used for production of phthalate plasticizers (i.e., esterification of an anhydride compound).

The process chemistry is based on an esterification reaction between trimellitic anhydride (TMA) and an alcohol (C_7 to C_{12}) to produce the corresponding ester and by-product water. The overall chemical reaction is shown below:

Trimellitic anhydride — Trimellitate — By-product water

A generalized process flow sheet for domestic production of trimellitic plasticizers is shown in Figure V-3. The liquid raw materials, consisting of TMA and an alcohol, are fed in the desired proportions along with a catalyst into an esterification reactor. A stoichiometric excess of alcohol is commonly used. A single catalyst is generally used, either a proton acid type such as toluenesulfonic acid, or a tetra alkyl titanate compound, which is amphoteric. In Figure V-3, it is assumed that an acid catalyst is used. Reactor effluent is sent directly to a wash tank system, and the acid catalyst,



Source: Midwest Research Institute

Figure V-3. Schematic flow diagram for production of trimellitate plasticizers.

along with a small amount of unconverted trimellitic anhydride, is separated from the crude product. The washed reaction product is then transferred to a batch-operated steam stripper, where unreacted alcohol (along with some water) is removed overhead and condensed. The stripper condensate is then treated in a decanter-type separator system to remove water from the alcohol. Recovered alcohol is reclaimed from a storage tank and recycled to the esterification reactor. Wastewater from the washing operation is combined with separated water from the decanter-separator system and sent to secondary treatment and disposal. An alternative stripping operation consists of a continuous distillation unit in which the washed reaction product is contacted countercurrently with steam.

Crude product discharged from the stripper is then treated in a multipurpose filtering operation to neutralize any residual traces of acid, remove suspended solids and clarify the final product material. Calcium oxide (CaO) is commonly used as a neutralizing material (e.g., as a precoat on the filter media). Filter aids are also commonly used (e.g., clay or diatomaceous earth). The filter cake is normally disposed as a solid waste material or used in the compounding of PVC resins. The finished product, which generally has a purity in excess of 99.5%, is then transferred to packaging and shipping operations.

By-Products and Contaminants--

The data compiled from manufacturers for product specifications indicate a general product purity for trimellitic acid esters of 99.5% or higher. The principal contaminants in the finished product generally consist of unreacted or partially reacted starting material and, in some cases, traces of catalyst residue. Although the catalyst is generally removed by chemical reaction, some traces may remain with the trimellitate final product.

The by-products of this reaction sequence consist of water of esterification and partial esters formed in the first process step. The water is separated during the reaction step in the esterification reactor and during the subsequent steam stripping step. Only trace amounts of the trimellitate are carried over with the water during the stripping process. The partial esters are removed during the final neutralization/clarification step.

Production Losses--

The overall loss of plasticizer due to processing and transfer of trimellitic acid esters results primarily from the catalyst removal procedure, the steam sparging process, and the final filtration. No data were found in the literature concerning specific percentage losses from each of these sources. Because the basic processing and transfer procedures employed for the trimellitates are very similar to those for epoxy compounds and linear polyesters, the percentage losses may be very similar. Overall processing and transfer losses for epoxy compounds and linear polyesters were estimated by the manufacturers to be approximately 2% of the production quantity. These losses occur in processes such as fractionation, steam stripping, filtration, neutralization, and washing. Since the same processes are employed in the manufacture of the trimellitates, it is estimated that approximately the same overall percentage loss should occur.

During processing of the previous two classes of plasticizers, the filtration step was estimated by manufacturers to account for the greatest loss, followed by the stripping (or sparging) procedure. Losses due to fractionation, neutralization, and washing were estimated by producers to be very small compared to the other methods of loss. For the trimellitate plasticizers, these same relative rankings would likely be valid.

Uses

Trimellitates are employed as primary plasticizers which require low volatility, low water extraction, low migration characteristics, good high temperature performance, and good electrical properties. No published data were available regarding the quantities of trimellitate used in specific areas. The following estimates of trimellitate consumption by use area were derived by MRI based on information supplied by various producers of the trimellitates: PVC 94-95%; ABS 1-2%; and miscellaneous 3-5%. Miscellaneous uses include other polymeric systems (e.g. chlorinated polyethylene, cellulose nitrate, cellulose acetate) and coating applications.

Within the very large consumption category of polyvinyl chloride (PVC), the applications are estimated to be as follows: 90% in communication cable coating and electrical wire and cable coating including 90°C and 105°C rated coatings; 2-3% bonded PVC and ABS rubber used in automotive and truck crash pads; 1% in speciality tapes and electrical tape; and 1% in plastisol uses for electrical purposes. The specialty tapes are often PVC-polyvinyl acetate copolymers.

Trimellitates are used as plasticizers in the ABS for automotive and truck panels and chlorinated polyethylene in high temperature, wire coating applications. Trimellitates are used in lacquers (coatings) to waterproof copper wiring in electric motors and generators.

Quantities Released During Processing--

Essentially all processes used with the high volume production of formulated PVC resins and synthetic rubber are highly automated and employ automatic equipment and pumping systems for liquid plasticizers. No information was available in the literature or from industry concerning quantities released during the formulation of resins or rubbers. Since the use of automated equipment usually precludes consistent loss, it is estimated that processing in the plastics and rubber industry does not lead to significant release of trimellitate plasticizer. Losses due to equipment malfunction or breakage occur but are very difficult to quantify.

Ultimate Disposal--

Although the useful life of plastics and other polymer products varies considerably from one product to another, most products will be discarded within a relatively short period of time (a few years). These products will be solid waste and subjected to either incineration or landfill. The very low volatility of the trimellitate plasticizers and their very low migration from plastics would preclude any appreciable loss of the plasticizer from the product during its use.

It has been estimated that of the phthalate plasticized plastics that are disposed as solid waste, an estimated 10-20% are destroyed by high temperature incineration and 2% are subjected to low temperature incineration or open burning (Peckall, 1975). The remainder of the plastic would be disposed in a landfill. Within the landfill, the trimellitate plasticizers are probably subject to attack by fungi and bacteria. The exact lifetime of the trimellitates in the landfill in unknown but based on the studies discussed in Section VI, the lifetime probably exceeds that for either the epoxy or polyester plasticizers.

Worker Exposure and Occupational Standards

Occupational Standards--

No information was found concerning any occupational standards for trimellitate plasticizers. Sources searched for these data were the National Institute for Occupational Safety and Health (1978a, 1978b), American Conference of Government Industrial Hygienists (1979), and Sittig (1979). A bulletin has been published concerning the health effects of trimellitic anhydride (TMA), the raw material for trimellitate production (NIOSH, 1978c).

Worker Exposure--

The National Institute for Occupational Safety and Health (1980) has estimated the total number of workers exposed to certain chemicals in plants of selected industries. No data were found for trimellitate plasticizers.

Environmental Transport and Degradation

Very few quantitative data were found for properties which would be directly related to environmental transport and bioaccumulation. Trimellitate plasticizers have very low vapor pressures at ambient conditions, about the same as the linear polyesters, so that volatility would not be a major factor in the transport through the environment. In addition, these plasticizers exhibit a very low solubility in water. No information was available on mobility in soils or sediments. No data were available for octanol-water partition coefficients so no inferences can be made with respect to bioaccumulation or biomagnification.

Environmental degradation can occur by photolysis, hydrolysis, and biological methods. No photolytic data were available nor have any studies been performed on degradation by microorganisms. In Section IV, conditions were discussed for the basic and acidic hydrolysis of trimellitate plasticizers.

SECTION VI

HEALTH AND ENVIRONMENTAL EFFECTS

HEALTH EFFECTS

This section summarizes the information available from the literature and manufacturers concerning the health effects of each of the three classes of plasticizers. In general, very few data were available in the literature for any of the three classes; no data were found for the trimellitates. Data from manufacturers normally stated only species tested, type of test, dosage level, and effects. Information was not available on testing protocol.

Epoxy Compounds

Many of the epoxy compounds have been approved by the Food and Drug Administration (FDA) for use as an indirect food additive. These additives are usually chemicals that constitute a relatively minor ingredient in the packaging materials, and contamination of foodstuffs would result from migration of the chemical from the packaging material into the food product. The FDA was contacted but they provided no information that had not been obtained from the literature.

Larson, et al. (1960) performed chronic toxicity studies on two epoxidized soybean oils, Paraplex G-60 and G-62 (products of Rohm and Haas). They performed two-year feeding studies at levels of up to 5% epoxidized oil in the diet of rats and one-year feeding studies in dogs at the same dietary levels.

In the study with Paraplex G-60, the highest dose (5%) produced relatively minor toxic effects in rats. These effects were manifest as early depression in weight gain and increased relative liver weight but no hepatic histopathology. The early depression in weight gain was recovered as the tests proceeded. A dose level of 2.5% did not produce any effects on the rats. The dogs appeared to be more sensitive to weight loss than the rats. Those dogs fed at the 5% level lost weight (or gained less than the controls) because they consumed less food than the controls due to an apparent aversion to the dosed feed. Those dogs fed at a dietary level of 1% oil were not adversly affected with respect to weight loss.

The results from Paraplex G-62 were similar but this product appeared to be somewhat more potent in its effects. Rats fed at a 1, 2.5, or 5% dietary level of the epoxidized oil had an initial depression of weight gain

but recovered later in the tests. Liver and kidney weights were increased, relative to the controls, in several of the higher dose groups; however since there was an absence of any significant histopathology, this result is of little toxicological importance. Dogs fed at the 5% dietary level lost weight in comparison to the controls, but those animals fed at the 1% level appeared to be normal with respect to weight levels.

In summary, the feeding study for Paraplex G-60 and G-62 on rats (two years) and dogs (one year) produced minimal nonspecific effects on weight gain, even at dietary levels of 5%. No effects were observed on survival and histologic examination of tissues of the heart, lung, liver, kidney, spleen, thyroid, adrenal, pancreas, gonads, muscle, and bone marrow showed no lesions attributable to treatment.

Weil, et al. (1963) conducted a massive study including preliminary acute toxicity tests on 60 compounds and skin-painting carcinogenesis studies on 28 of the compounds. Compounds of interest to this report included epoxidized soybean oil and seven epoxidized tall oil derivatives.

In the acute tests, all compounds of interest showed very little toxicity. Acute oral LD_{50} values for rats were in excess of 20 ml/kg body weight. Exposure of rats to the concentrated vapors for eight hours produced no deaths. Minimal skin irritation was produced on uncovered rabbit stomach. In an eye irritation test only one rabbit showed evidence of corneal injury from any of the eight compounds tested. None of the eight compounds showed any sensitization of guinea pigs. In the skin painting carcinogenesis study, neither the epoxidized soybean oil nor the two epoxidized tall oil esters produced any tumors.

In summary, the tested compounds were not totally inert, but they produced few toxic effects. These effects were limited to skin irritation effects even at relatively large doses.

Kotin and Falk (1963) reviewed the effects of various epoxides and peroxides and related materials on neoplasia, including incomplete mouse studies. Very few data were produced, and the data could not be evaluated due to a lack of control data. In addition, the loss of 60% of the test mice (30/50) during the course of the tests made evaluation of the results difficult.

Kieckebusch, et al. (1963) performed a structure-activity study of various epoxidized soybean oils. In this study, the degree of epoxidation (defined in terms of mg/epoxy oxygen/dose) was the independent variable. A dose-response relationship was found for weight gain and for death. In this study, no data were available to allow a comparison of the composition of these test materials with the commercial products currently on the market in the U.S. so that the results have no significant utility.

Arffman (1964) conducted a study of the effects of modified fats on newts as a potential screening method for carcinogenicity. The experimental methods for the animal testing were not described. The dependent variable

in the tests was epidermal reaction. Heat polymerized soybean oil produced negative results on the test species, and highly peroxidized oils showed a toxic effect. The compositions that are normal for commercial usage were negative.

Data from a producer for skin sensitivity for epoxidized soybean oil showed that patch tests on humans with undiluted epoxide for a 5-day period and 2-day repeat tests produced no irritation. A plastic film containing 19% epoxide patch tested on humans for 2 days with a repeat test of 4 days showed no cutaneous reactions (Rohm and Haas, 1980).

Linear Polyesters

Some of the linear polyesters available on the current market have been approved by the FDA as plasticizers for selected homopolymers used in contact with food. Information was solicited from FDA for seventeen specific linear polyesters, but information was available for only one compound, an azelaic acid-propylene glycol polymer. However, all data were designated as "privileged" and unavailable.

Only two reports were found in the literature on linear polyesters, Mallette and von Haam (1952) and Fancher, et al. (1973).

Mallette and von Haam (1952) conducted a study of the toxicity and skin effects of 25 plasticizers used in the rubber and plastics industries. Two linear polyesters, Paraplex G-25 and Paraplex G-40, were included in the study. For each of the two materials, intraperitoneal toxicity was negligible. Only one foreign body granuloma was found after a 6-g/kg injection. However, this study reported that when the two compounds were diluted in mineral oil or propylene glycol severe dermal irritation and moderate dermal sensitization effects were produced in humans. In the dermal irritation tests, they were the most toxic of all compounds tested. However, the latter results have been refuted by the manufacturer of the materials.

Information from the manufacturer, (Rohm and Haas, 1980) states that Paraplex G-25, either in undiluted form or as a 25% ointment, produced no skin irritation to human subjects after 48-hr contact. Tests employing 70% polyester in 30% toluol or 30% Solvesso 100 produced both skin irritation and sensitization due to the solvent. Tests using Paraplex G-40 as a 25% ointment produced no skin irritation to human subjects after a 48-hr contact period.

Fancher, et al. (1973) performed a two year chronic feeding study on rats and dogs and a three-generation reproduction study on rats using a 1,3-butylene glycol adipic acid polyester terminated by a 16% by weight mixture of myristic, palmitic, and stearic acids (Santicizer 334F). For all studies, the doses were 0, 0.1, 0.5, and 1.0% in the feed.

The toxicity tests showed no consistent toxic effects. A few parameters in the three-generation reproduction study were statistically different from the control animals, but there were no consistent effects over the course of the study. The overall results showed that there were no toxicological effects for this material in any of the chronic tests, even at a dose level of 1% in the feed.

Monsanto Company supplied unpublished toxicity information for five linear polyester plasticizers. The acute oral LD_{50} in rats was greater than 50 g/kg for Santicizer 409, greater than 10 g/kg for Santicizers 334F and 411, 9.42 g/kg for Santicizer 412, and 20.8 g/kg for Santicizer 429. Acute dermal LD_{50} for rabbits was estimated to be greater than 7.94 g/kg for Santicizers 334F and 411 and greater than 10 g/kg for the other three materials. Neither Santicizer 334F nor 411 showed eye irritation in rabbits; Santicizers 412 and 429 showed slight irritation, and Santicizer 409 showed mild irritation. Only Santicizer 411 showed slight skin irritation to rabbits for a 24-hr contact period; all others showed no irritation.

Rohm and Haas Company (1980) supplied toxicity information on three linear polyesters: Paraplex G-54, G-56, and G-57. The acute oral LD_{50} in rats was greater than 30 ml/kg for G-54 and greater than 5 ml/kg for G-56 and G-57. All three materials showed acute dermal LD_{50} levels in rabbits of greater than 3 g/kg. All three materials showed mild skin irritation to rabbits after a 24-hr contact period. Only G-57 showed mild eye irritation to rabbits; the other two produced no eye irritation. Patch tests of 24-hr duration conducted on 50 human subjects showed no signs of primary irritation or sensitivity reactions for Paraplex G-54.

Trimellitates

No information was available in the literature for this class of plasticizer. Data were supplied by two manufacturers of the trimellitate.

Monsanto Company provided information on Santicizer 79TM plasticizer. Acute oral LD_{50} in rats was found to be greater than 15.8 g/kg and acute dermal LD_{50} in rabbits was greater than 7.94 g/kg. Slight eye irritation was produced when the undiluted material was placed in the conjunctival sac of the rabbit. No skin irritation was detected on rabbits after a 24-hr contact period.

Eastman Kodak Company stated that their trioctyl trimellitate had oral and intraperitoneal LD_{50} greater than 3.2 g/kg in both rats and mice. Liquid placed in contact with guinea pig skin for 24 hr resulted in only slight irritation with no evidence of absorption (skin LD_{50} greater than 20 ml/kg). The skin of the guinea pig was also not sensitized during testing. During tests with rabbits slight eye irritation was produced by the undiluted material.

Rats survived a 6-hr exposure to 10 ppm of the trimellitate and exhibited only mild irritation. The animals gained weight in a normal manner during a two week observation period following exposure. However, rats exposed for 6-hr to calculated atmospheric concentrations of 118 ppm generated at 180°C resulted in death. These deaths were delayed for as long as three days.

The National Institute for Occupational Safety and Health (1978) has recommended that trimellitic anhydride (TMA) be handled as an extremely toxic agent. Exposure to this compound may result in noncardiac pulmonary edema (apparently without a pulmonary irritation warning), immunological sensitization, and irritation of the pulmonary tract, eyes, nose, and skin. It could be suggested that heating the trioctyl trimellitate to 180°C may have resulted in the thermal dissociation of a small amount of the ester to trimellitic anhydride. Therefore, the death of the rats may have resulted from inhalation of the anhydride and not from the trioctyl trimellitate.

ENVIRONMENTAL EFFECTS

No information was found in the literature concerning the effects of any of the three classes of plasticizers on fish, plants, birds, or mammals. Information was available relating to the effects of the epoxy compounds and linear polyesters on protista. The effects of two linear polyesters on fish have been studied by Monsanto Company. No environmental information was found for any of the trimellitates.

Effects on Fish

Unpublished data on the effects of two linear polyesters, Santicizer 409 and 429, were reported by Monsanto Company. In a 4-day static fish toxicity study using Santicizer 409, the 96-hr LD_{50} was calculated to be 100 ppm for fingerling rainbow trout and 125 ppm for bluegill.

A 4-day static study was also conducted for Santicizer 429. The 96-hr LD_{50} was calculated to be greater than 100 ppm for the fingerling rainbow trout and the bluegill.

Microbiological Degradation

Berk, et al. (1957) conducted a massive study in which 99 acids and their esters were among 127 compounds tested with 24 fungi. The object of the study was an attempt to correlate the extent of fungus growth with chemical structure. Among the compounds tested were two unidentified sebacic acid polyesters, polypropylene sebacate, and two materials identified only as polyesters. One of the unidentified sebacic acid polyesters was tied with another compound for the highest average fungal growth rate (6.8 cm) of all compounds tested. The other four polyesters also showed high fungal growth with average rates ranging from 5.1 to 6.0 cm. Only 21 of the 127 test compounds had average fungal growth rates in excess of 5.0 cm.

Klausmeier (1966) studied the isolation of microorganisms capable of degrading the ester plasticizers but incapable of using those esters as a sole source of nutrient and energy in a mineral salts medium. Butylene glycol polyadipate (BGA) was one of seven plasticizers used to isolate fungi. This compound (BGA) showed very poor fungal resistance with only 1 of 51 fungal isolates being adventitious (i.e., the isolate would degrade the plasticizer only in the presence of an extraneous organic nutrient). Bacterial and yeast cultures expected to be active against plastic materials were inoculated on yeast extract-BGA and mineral salt-BGA media. With the bacteria, BGA was

only adventitiously degraded; the yeast studies showed BGA to be adventitiously degraded in four of the tests and utilized as the sole organic nutrient in five of the tests.

Sterile strips of PVC film containing 50 parts of BGA per 100 parts of polymer were incubated in the presence of an undefined organism adventitiously capable of degrading BGA for various periods of time. The preliminary findings indicated that there was a considerable stiffening (loss of plasticizer) in the inoculated specimens after 23 days. No significant change occurred in the sterile controls.

Booth and Robb (1968) reported the bacterial attack on plasticized PVC in a soil environment for 8 weeks by species of Pseudomonas and Brevibacterium and the changes in some physical properties of the plastic that accompany the biodegradation process. Weight loss, cyclic deformation, and stress relaxation were the physical parameters tested.

Epoxidized soybean oil, with di-isooctyl phthalate (DIOP), and epoxy esters (plus DIOP) were the two epoxy compounds tested. Of 13 plasticizers in one test group, the two epoxy compounds ranked in approximately the middle in terms of weight loss and for the stiffness tests. They showed essentially no loss in the relaxation test. The relaxation test showed very little difference for all samples between the controls and the test material, so the results of this test provided very little guide to deterioration of all plasticizers tested. Overall, the epoxy compounds ranked in approximately the middle of 13 plasticizers for bacterial degradation during the course of this study.

Materials comprised of adipic acid plus propylene glycol and sebacic acid plus propylene glycol were the two linear polyesters tested. In the weight loss test and the stiffness test, the two polyesters ranked slightly above average out of 13 plasticizers. In the relaxation test, neither plasticizer showed any significant loss of relaxation. Overall, the polyesters were among the top five plasticizers in terms of bacterial degradation.

Darby and Kaplan (1968) tested three linear polyesters, both as monomers and as polymers with selected diisocynates, with six organisms for fungal susceptibility. The three linear polyesters were polyethylene glycol adipate, poly-1,3-propanediol adipate, and poly-1,4-butanediol adipate. The six fungi were: Aspergillus niger, A. flavus, A. versicolor, Penicillium funiculosum, Pullularia pullulans, and Trichoderma spp. (mixed species) with added Chaetomium globosum.

All polymers derived from each of the three polyesters were excellent substrates for fungal growth. All of the polymers except one showed heavy growth (60 to 100% covered). The exception showed moderate growth (30 to 60% covered). All three monomer polyesters showed heavy fungal growth.

Osmon, et al. (1969) studied the effects of 17 yeasts (8 different general) on 13 different plasticizers, including one polyester. Butylene glycol polyadipate (BGA) was the only material from the three classes of plasticizers of this survey. Of the 17 yeasts, 10 degraded the BGA regardless of the

presence of yeast extract as a nutrient; 3 yeasts were reverse adventitious (i.e., degraded plasticizer only in the absence of nutrient); and 4 yeasts showed no degradation.

Three of the cultures (Torulopsis BY4, Pullularia BY10, and Candida BY17) were selected for evaluation of their ability to degrade vinyl film, containing BGA, in liquid culture. After 14 days, none of the cultures significantly degraded the vinyl film even though all three cultures hydrolyzed BGA in the plate studies (described in the previous paragraph). Mixtures of cultures showed no improvement in the degradability of the vinyl film over the individual cultures.

Rodriquez (1971) published a review article on biodegradability of a number of components of plastics and rubber. Several of the previous articles on linear polyesters were briefly reviewed.

Lazar and Ioachimesca (1973) conducted a study in which a linear polyester, polypropylene glycol adipate, was among nine plasticizers subjected to testing for fungus attack. The polyester was among the most sensitive materials tested. The sample was completely covered by fungus mycelia and fructifications. Fungi employed in this study were not identified, Romanian and French standard methods were stated to have been employed.

Potts, et al. (1973a) studied the biodegradability of synthetic polymers. Polyvinyl chloride, containing epoxidized soybean oil plasticizer, was exposed to a mixture of fungi (A. niger, A. flavus, C. globosum, and P. funiculosum) for a period of 3 weeks. At the end of this period, the test sample showed medium growth with 30-60% of the sample covered with fungal growth.

Potts, et. al. (1973b) studied the biodegradability of commercially available plastics and additives commonly used in these plastics. The fungi and test methods were described in Pott, et al. (1973a). One epoxy plasticizer, epoxidized soybean oil (Flexol EPO), and one linear polyester, Plastolein 9765, were among the materials tested. Both plasticizers showed heavy fungal growth; each sample was 60 to 100% covered.

Sewage Treatment

Saeger, et al. (1976) studied the biodegradability of three aliphatic adipic acid diesters and one linear polyester, 1,3-butylene glycol adipic acid (Santicizer 334F), in acclimated, activated sludge systems. Carbon dioxide evolution procedures were employed to determine the biodegradability of the polyester. Primary biodegradation rates were not determined for this compound because of the lack of an applicable analytical method. At concentrations ranging from 20 to 56 mg/L, the extent of carbon dioxide evolution from the polyester was comparable to that for dextrose. For the two different carbon dioxide evolution procedures, gas evolution from the polyester after 35 days was 78.1 and 88.1% of theoretical, compared to 82.1 and 90.2% for Santicizer 97A, di(heptyl,nonyl) adipate, and 93.8 amd 96.4% for dextrose.

SECTION VII

PLASTICIZER INTERCHANGEABILITY

The entire concept of interchangeability among plasticizers within various resin systems is extremely complex and dependent upon the specific application for the particular product. A very large number of the plasticizers currently available on the market are basically directed towards specific uses or the incorporation of specific properties into a particular resin system. While general purpose plasticizers are commonly found on the market, the vast majority of the plasticizers are developed for specific purposes.

Data on plasticizer compatibility were compiled from the published literature (Modern Plastics Encyclopedia, 1979-80). Information presented in Table VII-1 relates to the overall compatibility of various classes of plasticizers with specific resins. The table is not comprehensive with respect to all classes of plasticizers but does incorporate all of the major classes. For those plasticizer classes which are stated to be not used with a resin, the data from the Modern Plastics Encyclopedia showed that none of the individual plasticizers within the specific class are used with the resin. Within each class of plasticizer, an estimate was made of the general compatibility of that class with the specific resin. This does not imply that all plasticizers within a certain class will conform to the compatibility rating given for the class. In addition, not all plasticizers within a given class may be used with a particular resin. For example, adipic acid esters as a class are partially compatible with polymethyl methacrylate. Some specific esters may be incompatible and some may be compatible; but overall, the majority of the specific esters are partially compatible. However, for azelaic acid esters, none of the specific esters are used with polymethyl methacrylate.

Tables VII-2 to VII-4 present general interchangeability information for each of the three classes of plasticizers in this study, i.e., epoxy, polyester, or trimellitate. In these tables, the resins which show compatibility with one of the three classes of plasticizers are compared with all other classes of compatible plasticizers. In Table VII-2, epoxy plasticizers are stated to be generally compatible with cellulose acetate butyrate, cellulose nitrate, ethyl cellulose, polyvinyl chloride, and vinyl chloride acetate. Numerous other classes of plasticizers are shown which are also compatible with these resins. As in Table VII-1, not all of the individual plasticizers within a given class are completely compatible with a specific resin. These data present generalizations for entire classes.

TABLE VII-1. GENERAL COMPATIBILITY OF PLASTICIZERS

Plasticizer	Compatibility with plastics[a]									
	CA	CAB	CN	EC	PM	PS	PVA	PVB	PVC	VCA
Adipic acid derivatives	P[b]	C	C	C	P	C	P	P	C	C
Azelaic acid derivatives	C	C	C	C	N	C	P	I	C	C
Benzoic acid derivatives	P	C	P	C	C	P	P	P	C	P
Polyphenyl derivatives	I	C	C	C	N	C	C	C	C	C
Citric acid derivatives	C	C	C	C	N	C	C	C	C	C
Epoxy derivatives	I	I	C	C	I	I	I	I	C	C
Fumaric acid derivatives	N	N	N	N	N	N	C	N	C	C
Glutaric acid derivatives	P	C	P	C	P	C	P	P	C	C
Glycerol derivatives	C	C	C	C	C	I	C	C	I	I
Glycol derivatives	I	C	C	C	C	C	C	C	C	C
Isophthalic acid derivatives	I	C	C	C	P	C	P	C	C	C
Lauric acid derivatives	N	C	C	C	N	C	N	C	C	C
Maleic acid derivatives	N	N	N	N	N	N	C	N	N	N
Trimellitates	I	C	C	C	C	P	I	P	C	C
Myristic acid derivatives	I	C	C	C	N	C	N	N	N	I
Oleic acid derivatives	I	C	C	C	P	C	P	C	C	P
Paraffin derivatives	C	C	P	C	C	C	C	P	C	C
Petroleum derivatives	I	I	I	C	C	C	C	P	P	C
Phosphoric acid derivatives	C	C	C	C	C	C	C	C	C	C
Phthalic acid derivatives	I	C	C	C	C	C	I	C	C	C
Polyesters	I	C	C	I	I	I	P	I	C	C
Ricinoleic acid derivatives	I	C	C	C	P	P	C	C	C	C
Sebacic acid derivatives	I	P	C	C	C	C	P	P	C	C
Stearic acid derivatives	I	C	C	C	I	C	C	C	C	C
Sucrose derivatives	C	C	C	C	C	C	C	I	C	C
Sulfonic acid derivatives	C	C	C	C	C	P	C	C	I	C
Tall oil derivatives	P	N	P	C	N	N	P	C	C	C
Terephthalic acid derivatives	I	C	C	P	N	C	C	P	C	C

[a] Code for Plastics: CA=Cellulose acetate; CAB=Cellulose acetate butyrate; CN=Cellulose nitrate; EC=Ethyl cellulose; PM=Polymethyl methacrylate; PS=Polystyrene; PVA=Polyvinyl acetate; PVB=Polyvinyl butyral; PVC=Polyvinyl chloride; VCA=Vinyl chloride acetate.

[b] Code for Compatibility: C=Compatible; P=Partially compatible; I=Incompatible; N=Not used in this plastic.

TABLE VII-2. INTERCHANGEABILITY FOR EPOXY PLASTICIZERS

Plasticizers	Compatible plastics[a]				
	CAB	CN	EC	PVC	VCA
Epoxy derivatives	C	C	C	C	C
Adipic acid derivatives	C[b]	C	C	C	C
Azelaic acid derivatives	C	C	C	C	C
Benzoic acid derivatives	C		C	C	
Polyphenyl derivatives	C	C	C	C	C
Citric acid derivatives	C	C	C	C	C'
Fumaric acid derivates				C	C
Glutaric acid derivatives	C		C	C	C
Glycerol derivatives	C	C	C		
Glycol derivatives	C	C	C	C	C
Isophthlaic acid derivatives	C	C	C	C	C
Lauric acid derivatives	C	C	C	C	C
Trimellitates	C	C	C	C	C
Myristic acid derivatives	C	C	C		
Oleic acid derivatives	C	C	C	C	
Paraffin derivatives	C		C	C	C
Petroleum derivatives			C		C
Phosphoric acid derivatives	C	C	C	C	C
Phthalic acid derivatives	C	C	C	C	C
Polyesters	C	C		C	C
Ricinoleic acid derivatives	C	C	C	C	C
Sebacic acid derivatives		C	C	C	C
Stearic acid derivatives	C	C	C	C	C
Sucrose derivatives	C	C	C	C	C
Sulfonic acid derivatives	C	C	C		C
Tall oil derivatives			C	C	C
Terephthalic acid derivatives	C	C		C	C

[a] Code for Plastics: CAB=Cellulose acetate butyrate; CN=Cellulose nitrate; EC=Ethyl cellulose; PVC=Polyvinyl chloride; VCA=Vinyl chloride acetate.

[b] C=Compatible.

TABLE VII-3. INTERCHANGEABILITY FOR POLYESTER PLASTICIZERS

Plasticizer	Compatible plastics[a]			
	CAB	CN	PVC	VCA
Polyesters	C[b]	C	C	C
Adipic acid derivatives	C	C	C	C
Azelaic acid derivatives	C	C	C	C
Benzoic acid derivatives	C		C	
Polyphenyl derivatives	C	C	C	C
Citric acid derivatives	C	C	C	C
Epoxy derivatives		C	C	C
Fumaric acid derivatives			C	C
Glutaric acid derivatives			C	C
Glycerol derivatives	C	C		
Glycol derivatives	C	C	C	C
Isophthalic acid derivatives	C	C	C	C
Lauric acid derivatives	C	C	C	C
Trimellitates	C	C	C	C
Myristic acid derivatives	C	C		
Oleic acid derivatives	C	C	C	
Paraffin derivatives	C		C	C
Petroleum derivatives				C
Phosphoric acid derivatives	C	C	C	C
Phthalic acid derivatives	C	C	C	C
Ricinoleic acid derivatives	C	C	C	C
Sebacic acid derivatives		C	C	C
Stearic acid derivatives	C	C	C	C
Sucrose derivatives	C	C		C
Sulfonic acid derivatives	C	C		C
Tall oil derivatives				C
Terephthalic acid derivatives	C	C	C	C

[a] Code for Plastics: CAB=Cellulose acetate butyrate; CN=Cellulose nitrate; PVC=Polyvinyl chloride; VCA=Vinyl chloride acetate.

[b] C=Compatible.

TABLE VII-4. INTERCHANGEABILITY FOR TRIMELLITATE PLASTICIZERS

Plasticizer	Compatible plastics[a]					
	CAB	CN	EC	PM	PVC	VCA
Trimellitates	C[b]	C	C	C	C	C
Adipic acid derivatives	C	C	C		C	C
Azelaic acid derivatives	C	C	C		C	C
Benzoic acid derivatives	C		C	C	C	
Polyphenyl derivatives	C	C	C		C	C
Citric acid derivatives	C	C	C		C	C
Epoxy derivatives	C	C	C		C	C
Fumaric acid derivatives					C	C
Glutaric acid derivatives	C		C		C	C
Glycerol derivatives	C	C	C	C		
Glycol derivatives	C	C	C	C	C	C
Isophthalic acid derivatives	C	C	C		C	C
Lauric acid derivatives	C	C	C		C	C
Myristic acid derivatives	C	C	C			
Oleic acid derivatives	C	C	C		C	C
Paraffin derivatives	C		C	C	C	C
Petroleum derivatives			C	C		C
Phosphoric acid derivatives	C	C	C	C	C	C
Phthalic acid derivatives	C	C	C	C	C	C
Polyesters	C	C			C	C
Ricinoleic acid derivatives	C	C	C		C	C
Sebacic acid derivatives		C	C	C	C	C
Stearic acid derivatives	C	C	C		C	C
Surcose derivatives	C	C	C	C	C	C
Sulfonic acid derivatives	C	C	C	C		C
Tall oil derivatives			C		C	C
Terephthalic acid derivatives	C	C			C	C

[a] Code for Plastics: CAB=Cellulose acetate butyrate; CN=Cellulose nitrate; EC=Ethyl cellulose; PM=Polymethyl methacrylate; PVC=Polyvinyl chloride; VCA=Vinyl chloride acetate.

[b] C=Compatible.

An evaluation of specific plasticizer usage and interchangeability on an individual plasticizer basis would be extremely complex because of the many factors which are involved in the selection of a plasticizer for a particular resin. Physical properties of the plasticizer, resin component compatibility, physical properties of the resultant plastic, effect on product specifications, and overall process economics are a few of the factors which must be considered if a change of a specific plasticizer for a specific resin is contemplated. An evaluation of all possible alternatives for each individual plasticizer for each specific application is beyond the scope and intent of this study.

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